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Reaction of Sugar Esters with Hydrogen Fluoride

IX. Derivatives of 2-*O*-Methyl-D-xylose and 2-*O*-Methyl-D-arabinose

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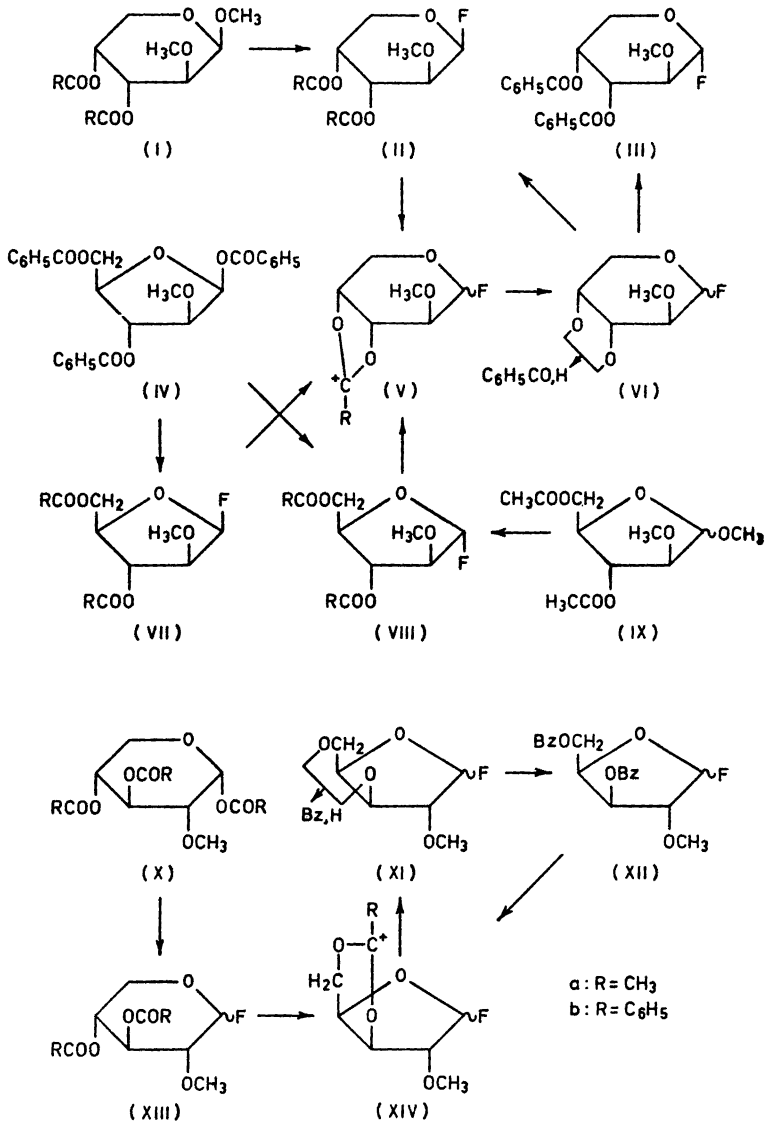
Brief treatment of methyl 3,4-di-*O*-benzoyl-2-*O*-methyl-β-D-arabinopyranose (Ib) with anhydrous hydrogen fluoride gave the corresponding pyranosyl fluoride (IIb). On more prolonged reaction with hydrogen fluoride (IIb) was converted to a dioxolanylium ion (Vb), derived from 2-*O*-methyl-D-arabinopyranosyl fluoride. Analogous treatment of 1,3,5-tri-*O*-benzoyl-2-*O*-methyl-β-D-arabinofuranose (IV) with hydrogen fluoride gave the furanosyl fluoride (VIIb) which on further reaction underwent ring-expansion to give (Vb). Reaction of 1,3,5-tri-*O*-benzoyl-2-*O*-methyl-α-D-xylopyranose (Xb) with hydrogen fluoride first gave the corresponding fluoride (XIII) which, on more prolonged reaction, underwent ring-contraction to the dioxolanylium ion (XIVb), derived from 2-*O*-methyl-D-xylofuranosyl fluoride. The ion (XIVb) was also formed when 3,5-di-*O*-benzoyl-2-*O*-methyl-D-xylofuranosyl fluoride (XII) was treated with hydrogen fluoride. Similar experiments were carried out with the corresponding acetates. All the reactions were followed by NMR spectroscopy of the hydrogen fluoride solutions.

Hydrogen fluoride induced epimerization of carbohydrate esters is a rather general reaction.[1] In some cases it has also been found that acylated glycopyranoses may undergo ring contraction to yield furanose derivatives by treatment with anhydrous hydrogen fluoride. Thus the tetrabenzoates of ribopyranose and arabinopyranose are both completely converted to ribofuranose derivatives by prolonged treatment with hydrogen fluoride.[2] Tetra-*O*-benzoyl-2-*O*-methyl-D-glucopyranose is partly rearranged to a 2-*O*-methylglucofuranose derivative by reaction with hydrogen fluoride for 24 h.[3] Tetra-*O*-benzoyl-D-xylopyranose, on the other hand, is rearranged to 2,4-di-*O*-benzoyl-D-arabinopyranose; no furanose derivatives are formed.[2] In order to gain insight into the factors affecting the pyranose to furanose rearrangement the behaviour of a number of *O*-methylated carbohydrate derivatives has been studied and in the present paper the reaction of 2-*O*-methyl-D-arabinose and 2-*O*-methyl-D-xylose derivatives with hydrogen fluoride is described.



Treatment of methyl 3,4-di-*O*-benzoyl-2-*O*-methyl-β-D-arabinopyranoside (Ib) with anhydrous hydrogen fluoride for 10 min gave a 70 % yield of 3,4-di-*O*-benzoyl-2-*O*-methyl-β-D-arabinopyranosyl fluoride (IIb); the α-anomer (III) was not formed. Analogously, brief treatment of the diacetate (Ia) with hydrogen fluoride yielded the acetylated fluoride (IIa).

NMR spectra of the hydrogen fluoride solutions showed that the fluorides (IIa and IIb) were formed immediately when (Ia) and (Ib), respectively, were

Table 1. Chemical shifts (in ppm relative to $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$) and coupling constants (Hz) of the ions (V) and (XIV) in anhydrous hydrogen fluoride at 60 Mc.

Compound	H_1	H_2	H_3	H_4	H_{5a} H_{5e}	OCH_3	H_3C-^+C	H_3CCOOH	J_{12}	J_{1F}	J_{2F}	J_{23}	J_{34}
α-Va	5.86		5.9–6.0	4.5–4.6		3.75	2.83	2.55	3.2	55			
β-Va	5.94		5.9–6.0	4.5–4.6		3.81	2.90	2.55	3.5	52			
α-Vb	5.90		6.1–6.25	4.65–4.8		3.80			3	52			
β-Vb	6.02		6.1–6.25	4.65–4.8		3.95			3.5	52.5			
β-XIVa	6.03	4.6	5.72		5.2	3.78	2.73	2.5	~0	61	3.5		4.0
β-XIVb	6.09	4.85	5.97		5.4	3.92			~0	60	4.0	<0.5	4.2

dissolved in hydrogen fluoride. The spectra also showed that when the hydrogen fluoride solutions, containing (IIa) or (IIb), were kept at room temperature further reactions took place and after 5 and 24 h, respectively, the initially formed fluorides were completely transformed into the dioxolanylium ions (Va) and (Vb). The NMR data of these ions are given in Table 1. The signals at 2.83 and 2.90 ppm of the acetates show that acetoxonium ions are formed and the signal at 2.55 ppm shows that one equivalent of acetic acid has been cleaved off. The ions (V) did not undergo further reaction when kept for several days in hydrogen fluoride solution. It may be noted that a mixture of anomers of the ions (V) are formed whereas brief treatment of (Ia or b) with hydrogen fluoride only gave the β-anomers (IIa and b). When the hydrogen fluoride solution containing (Vb) was worked up a mixture of the anomeric mono-*O*-benzoyl-2-*O*-methyl-D-arabinopyranosyl fluorides (VI) were obtained in an α : β ratio of *ca.* 1 : 3, as seen from the NMR spectra. Benzoylation of this mixture gave (IIb) and 3,4-di-*O*-benzoyl-2-*O*-methyl-α-D-arabinopyranosyl fluoride (III).

The formation of a dioxolanylium ion (V) from the *cis*-oriented acyloxy groups of (II) is in agreement with previous results.[1,4] In the furanose derivative, 1,3,5-tri-*O*-benzoyl-2-*O*-methyl-β-D-arabinofuranose (IV), the benzoyl-groups are *trans*-oriented and they would therefore not be expected to form any cyclic ion unless rearrangement takes place.[8] Brief treatment of (IV) with hydrogen fluoride gave as expected the anomeric furanosyl fluorides (VIIb) and (VIIIb). When (IV) was kept in hydrogen fluoride for several days the initially formed furanosyl fluorides, (VIIb) and (VIIIb), disappeared, as seen from the NMR spectra, and the anomeric ions (IVb) were formed. Work up of the hydrogen fluoride solution after 4 days at room temperature and benzoylation of the crude product gave the anomeric pyranosyl fluorides (IIb) and (IIIb). NMR spectra of a hydrogen fluoride solution of methyl 3,5-di-*O*-acetyl-2-*O*-methyl-D-arabinofuranoside (IX) also showed that the initially formed fluorides, (VIIa) and (VIIIa), were converted into the acetoxonium ion (Va) in the course of 24 h.

The conversion of (IV) to (V) is the first example of a hydrogen fluoride induced ring expansion to be found. It seems likely that the interconversion of pyranoses and furanoses in hydrogen fluoride is a reversible reaction, and

that the equilibrium is determined by the stability of the products. Dioxolanylium ions are found to be rather stable in hydrogen fluoride and the behaviour of the 2-*O*-methyl-D-arabinose derivatives, described above, is probably determined by this fact. The pyranose derivatives can form the only possible dioxolanylium ion (V) directly, whereas the furanose derivatives has to undergo ring expansion in order to give this ion.

Tri-*O*-benzoyl-2-*O*-methyl-D-xylopyranose (Xb), or the corresponding triacetate (Xa), have the acyloxy-groups at C-3 and C-4 *trans*-oriented and cannot form dioxolanylium ions as such. They would therefore be expected to undergo ring contraction by prolonged reaction with hydrogen fluoride to give furanose derivatives which can form the ions (XIV).

Brief treatment of (Xb) with hydrogen fluoride gave a good yield of di-*O*-benzoyl-2-*O*-methyl-α-D-xylopyranosyl fluoride (α-XIIIb) together with a small amount of the β-anomer. When (Xb), or the acetate (Xa), were dissolved in hydrogen fluoride the fluorides (XIIIb) and (XIIIa), respectively, were formed immediately as seen from the NMR spectra. When the hydrogen fluoride solutions were kept at room temperature, or at 0°, further reactions took place and spectra showed that after *ca.* 25 h at room temperature (Xa) and (Xb) had formed the ions (XIVa) and (XIVb), respectively. Thus the spectra derived from (Xa) showed that two equivalents of acetic acid had been cleaved off and a signal corresponding to an acetoxonium ion had appeared at 2.73 ppm. Further spectral data of (XIVa and b) are given in Table 1. Work up of a solution of (XIVb) in hydrogen fluoride gave a crude product which probably consisted of a mixture of monobenzoylated 2-*O*-methyl-D-xylo-

Table 2. First order chemical shifts (δ-values and

ompound	Solvent	H_1	H_2	H_3	H_4	H_5	H_5'	$-OCH_3$
a	C_6H_6	4.77	3.72	5.55	5.41	3.48	3.39	3.10, 3.18
b	$CDCl_3-C_6H_6$ 1 : 4	4.87	3.95	5.83	5.71	3.65	3.62	3.21, 3.25
Ia	$CDCl_3$	5.79	3.69	5.26	5.38	4.10	3.83	3.53
Ib	$CDCl_3-CH_3COCH_3$ 1 : 3	6.02	4.10	5.62	5.76	4.34	4.09	3.57
II	$CDCl_3-CH_3COCH_3$ 1 : 1	5.55	3.77	5.69	5.57	4.01	4.37	3.59
-VIb	$CDCl_3-C_6H_6$ 3 : 2	5.66	3.50	3.9–4.1	4.30	4.8		3.30
V	C_6H_6	6.77	3.95	5.90	4.32	4.68	4.84	3.08
IIb	$CDCl_3-C_6H_6$ 1 : 2	5.56	3.86	5.69	4.27	4.54	4.75	3.54
IIIb	CH_3COCH_3	5.91	4.22	5.45	4.81	4.59	4.65	3.54
IX	CD_3COCD_3	4.90	3.72	4.95		3.9 —— 4.5		3.34, 3.38
-IX	C_6D_6	4.66	3.75	5.41	4.09	4.33	4.60	3.09, 3.21
a	CD_3COCD_3	5.61	3.33	5.17	4.86	4.01	3.53	3.46
b	$CDCl_3$	6.17	3.74	5.71	5.36	4.44	3.85	3.58
XII	$CDCl_3$	5.91	4.22	5.78	4.98	4.48		3.52
-XII	$CDCl_3$	5.84	4.13	5.69	4.96	4.70		3.59
XIIIb	$CDCl_3$	5.83	3.62	5.95	5.36	4.19	3.96	3.52
-XIIIb	$CDCl_3$	5.59	3.57	5.60	5.28	4.47	3.92	3.56

In pyranose $H_5=H_{5e}$ and $H_5'=H_{5a}$.

furanosyl fluorides (XI). Benzoylation of this product gave the 3,5-di-*O*-benzoyl-2-*O*-methyl-α- and β-D-xylofuranosyl fluorides (XII). The two anomers were separated and their structures were determined through their NMR spectra (Table 2).

When (XII) was dissolved in hydrogen fluoride and kept at 0°C for 24 h it gave the ion (XIVb) as seen from the NMR spectrum, which was identical with that obtained from (Xb) in hydrogen fluoride. The formation of (XIV) from (X) or (XII) is accompanied by some decomposition as seen from the dark colour of the hydrogen fluoride solution. The ion (XIV) is stable in hydrogen fluoride solution for several days. Since (XII) can yield (XIV) it has no tendency to undergo ring-expansion in hydrogen fluoride, in contrast to the 2-*O*-methyl-D-arabinofuranose derivatives mentioned above.

The NMR spectral data of the compounds prepared in the present investigation are presented in Table 2. The structures are easily deduced from the NMR data. The F – H coupling constants agree with those found for other furanosyl fluorides.[5] When F-1 and H-2 are *trans*-oriented $J_{F1,H2}$ is *ca.* 20 Hz (compounds VIIb and α-XII) whereas a *cis*-orientation of these two atoms results in a coupling constant of *ca.* 6 Hz (compounds VIIIb and β-XII). The configurational dependence of the long-range coupling between F-1 and H-4, which was observed previously,[5] has also been found in the present compounds. Thus a *trans*-relationship between F-1 and H-4 gives a coupling constant of *ca.* 6 Hz (compounds VIIb and β-XII), whereas a *cis*-arrangement gives a much smaller value of $J_{F1,H4}$ (compounds VIIIb and α-XII).

coupling constants (Hz)) deduced from 100 Mc NMR spectra.

OAc		J_{12}	J_{23}	J_{34}	J_{45}	J_{45}'	J_{55}'	J_{1F}	J_{2F}	J_{4F}		Predominant conformation
1.74,	1.76	3.4	9.8	3.4	1.6	1.9	12.9					$^1C_4$
		3.4	9.6	3.4	1.5	1.6	12.8					$^1C_4$
2.06,	2.15	2.6	10.4	3.5	1.2	1.8	12.8	51.5	24.3	~0	J_{15} ~0.5	$^1C_4$
		2.6	10.2	3.5	1.5	2.0	13.2	53.0	24.0	~0		$^1C_4$
											J_{35e} ~0.9	
		2.8	5.1	3.5	4.3	7.9	11.3	49.5	5.7	~0	J_{35a} ~1.3	$^4C_1$
		3–4	10	3–4	<2	<2		53	25			$^1C_4$
		4.5	6.6	5.3	6.1	4.6	11.2					
		3.5	6.6	5.4	5.6	3.8	11.5	63.8	20.3	6.0		
		<0.5	0.8	3.2	5.4	3.8	11.5	59.2	6.8	1.5	J_{3F} ~0.5	
2.01,	2.05	0.7	1.9									
1.59,	1.74	4.3	7.0	5.2	7.2	3.9	11.1					$^4C_1$
		7.2	8.7	8.7	5.0	9.0	11.7					
		5.6	6.8	7.0	4.4	7.1	12.0					$^4C_1$
		3.6	6.2	6.7	5.9	5.9		62.5	18.0	≤1		
		~0	<1	5.2	5.5	6.5		62.6	5.9	6		
		2.8	9.8	9.8	6.0	11.0	11.3	52.2	24.5	<1		$^4C_1$
		3.0	5.1	5.3	3.1	4.2	12.8	51.3	9			$^1C_4$

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were obtained on Varian A-60 and HA-100 instruments using tetramethylsilane as internal reference. For thin layer chromatography (TLC) silica gel PF_{254} (Merck) was used. Preparative TLC was done with 1 mm thick layers on 20 × 40 cm plates. Zones were detected under UV light (benzoates) or by charring with a hot wire (acetates).

2-*O*-Methyl-arabinose derivatives

*Methyl 3,4-di-*O*-acetyl-2-*O*-methyl-β-*D*-arabinopyranoside (Ia).* Methyl 2-*O*-methyl-β-D-arabinopyranoside [6] (6.2 g) was acylated in the usual manner with acetic anhydride (8 ml) in pyridine (25 ml). The crude product (6.9 g) was a slightly yellow syrup which was purified by molecular distillation (evaporator 100–120°, 10^{-3} mmHg) to give 5.3 g (55 %) of pure (Ia) as a colourless syrup, $[\alpha]_D^{24} = -184°$ (*c* 0.9, $CHCl_3$) (reported [7] for the L-enantiomer: $[\alpha]_D^{21} = +186°$C). (Found: C 50.44; H 6.71. Calc. for $C_{11}H_{18}O_7$: C 50.37; H 6.92.)

*Methyl 3,4-di-*O*-benzoyl-2-*O*-methyl-β-*D*-arabinopyranoside (Ib.)* Benzoylation of methyl 2-*O*-methyl-β-D-arabinopyranoside (2.9 g) with benzoyl chloride (5 ml) in pyridine (20 ml) gave 6.0 g of a brown syrup. Chromatography on a column of silica gel (400 g) using benzene–ether (1 : 1) as eluent gave 3.4 g (54 %) of a colourless syrup which crystallized on standing. Two recrystallizations from ether–pentane gave pure (Ib), m.p. 75–77°C $[\alpha]_D^{20} = -263°$ (*c* 1.8, $CHCl_3$). (Found: C 65.03; H 5.67. Calc. for $C_{21}H_{22}O_7$: C 65.27; H 5.74.) Direct crystallization of (Ib) without chromatography gave *ca.* 40 % of a product with m.p. 75–77°.

*Methyl 3,5-di-*O*-acetyl-2-*O*-methyl-D-arabinofuranosides (IX).* A solution of 2-*O*-methyl-D-arabinose [6] (1.7 g) in 100 ml of 1 % methanolic hydrogen chloride was kept at room temperature until it no longer reduced Fehlings solution (4.5 h). Pyridine (15 ml) was then added and the solvents were removed *in vacuo*. The residue was evaporated twice with pyridine to remove the methanol. It was then acetylated with acetic anhydride (2.5 ml) in pyridine (50 ml). Work up in the usual way gave 2.4 g of a colourless syrup which was shown by GLC to contain four components in about equal amounts. Preparative GLC of 600 mg of the mixture (150 μl of a 50 % ether solution was injected at a time on a 1 m column of 20 % silicone elastomer (E 301) on Chromosorb P at 165°) gave four fractions. The first fraction consisted of 65 mg of methyl 3,5-di-*O*-acetyl-2-*O*-methyl-α-D-arabinofuranoside (α-IX), $[\alpha]_D^{21} = +83°$ (*c* 0.6, $CHCl_3$). (Found: C 49.85; H 6.88. Calc. for $C_{11}H_{18}O_7$: C 50.37; H 6.92.) The next fraction gave 95 mg of the corresponding β-anomer (β-IX). The product crystallized from ether–pentane, m.p. 48.5–49°C, $[\alpha]_D^{21} = -101°$ (*c* 0.8, $CHCl_3$). (Found: C 50.35; H 6.91.) The following two fractions were discarded since NMR spectra showed that they were complicated mixtures.

*1,3,5-Tri-*O*-benzoyl-2-*O*-methyl-β-*D*-arabinofuranose (IV).* 1,3,5-Tri-*O*-benzoyl-β-D-arabinofuranose [8] (2.5 g) was methylated with diazomethane and boron trifluoride.[9] Chromatography of the product (2.7 g) on a column of silica gel (250 g) using ether–pentane–methylene chloride (9 : 9 : 2) as eluent followed by crystallization from ether–pentane gave 300 mg (12 %) of pure (IV), m.p. 109–110°C, $[\alpha]_D^{21} = -19.0°$ (*c* 1.4, $CHCl_3$). (Found: C 67.95; H 5.11. Calc. for $C_{27}H_{24}O_8$: C 68.06; H 5.08.) The mother liquors gave 1.3 g (50 %) of a less pure product, m.p. 107–109°C.

Reactions with hydrogen fluoride

*Methyl 3,4-di-*O*-benzoyl-2-*O*-methyl-β-*D*-arabinopyranoside (Ib)* (500 mg) was dissolved in anhydrous hydrogen fluoride (1 ml) at 0°C and kept for 10 min. Methylene chloride was then added and the mixture was poured unto ice. The organic layer was washed with aqueous sodium hydrogen carbonate, dried and evaporated. The product (493 mg) was purified by preparative TLC using ether–pentane (1 : 2) as eluent to give 340 mg (70 %) of 3,4-di-*O*-benzoyl-2-*O*-methyl-β-D-arabinopyranosyl fluoride (IIb) as a colourless syrup, $[\alpha]_D^{22} = -248°$ (*c* 2.0, $CHCl_3$). (Found: 64.06; H 5.25. Calc. for $C_{20}H_{19}O_6F$: C 64.16; H 5.12.)

Treatment of (Ib) (1.04 g) with hydrogen fluoride (2 ml) for 48 h at room temperature gave 824 mg of a brown syrup. Preparative TLC (ether – pentane 2 : 1) gave, in addition to methyl benzoate, two fractions. The fastest running fraction (50 mg) consisted of at least three products and was not investigated further. The second fraction (346 mg) consisted of a mixture of 3 parts of 4-*O*-benzoyl-2-*O*-methyl-β-D-arabinopyranosyl fluoride and 1 part of an α-fluoride as seen from an NMR spectrum. The mixture was benzoylated and the product was separated into two fractions by preparative TLC (ether – pentane 1 : 2). The slower moving fraction gave 297 mg (29 %) of 3,4-di-*O*-benzoyl-2-*O*-methyl-β-D-arabinopyranosyl fluoride (IIb), identical with the product described above. The fast running fraction yielded the corresponding α-fluoride (III) as a colourless syrup, 52 mg (5 %), $[\alpha]_D^{21} = +20.7°$ (*c* 0.4, $CHCl_3$). (Found: C 64.07; H 5.10. Calc. for $C_{20}H_{19}O_6F$: C 64.16; H 5.12.)

In a similar experiment (Ib) (1.006 g) was treated with hydrogen fluoride for 48 h giving 621 mg of crude (VI), which was benzoylated without previous purification. Preparative TLC of the product gave 116 mg (12 %) of (III) and 430 mg (44 %) of (IIb).

1,3,5-Tri-O-*benzoyl-2*-O-*methyl*-β-D-*arabinofuranose* (*IV*). Treatment of (IV) (311 mg) with anhydrous hydrogen fluoride (1 ml) for 5 min at room temperature and work up as described above gave 247 mg of crude product. This was separated into two fractions by preparative TLC using ether – pentane (1 : 1) as eluent. The fastest running fraction gave 143 mg (58 %) of 3,5-di-*O*-benzoyl-2-*O*-methyl-α-D-arabinofuranosyl fluoride (VIII) as a syrup, $[\alpha]_D^{21} = +49.3°$ (*c* 0.5, $CHCl_3$). (Found: C 64.02; H 5.20. Calc. for $C_{20}H_{19}O_6F$: C 64.16; H 5.12.) The slow moving fraction gave 55 mg (22 %) of the corresponding β-anomer (VII), m.p. 112 – 115°C. Two recrystallizations from ether – pentane gave the pure product, m.p. 115 – 116°C, $[\alpha]_D^{21} = +13.2°$ (*c* 1.0; $CHCl_3$). (Found: C 64.05; H 5.16.)

When (IV) (235 mg) was treated with hydrogen fluoride for 4 days at room temperature 101 mg of crude (VI) was obtained. This was benzoylated and the product was separated into two fractions by preparative TLC (ether – pentane 2 : 1). These consisted of (III) (23 mg, 12 %) and (IIb) (53 mg, 29 %). Both products were identified by NMR spectroscopy.

Methyl 3,4-di-O-*acetyl-2*-O-*methyl*-β-D-*arabinopyranoside* (*Ia*). A solution of (Ia) (970 mg) in hydrogen fluoride (2 ml) was kept at 0°C for 5 min and worked up as described above. The crude product (720 mg), m.p. 60 – 75°C, was recrystallized from ether – pentane to give 535 mg (58 %) of 3,4-di-*O*-acetyl-2-*O*-methyl-β-D-arabinopyranosyl fluoride (IIa), m.p. 77 – 79°C, $[\alpha]_D^{22} = -171°$ (*c* 0.64; $CHCl_3$). (Found: C 48.10; H 6.04. Calc. for $C_{10}H_{15}O_6F$: C 48.00; H 6.04.)

2-*O*-Methyl-D-xylose derivatives

Tri-O-*benzoyl-2*-O-*methyl*-α-D-*xylopyranose* (*Xb*). 2-*O*-Methyl-D-xylose [10,11] (3.0 g) was added in the course of 30 min to a stirred mixture of pyridine (30 ml) and benzoyl chloride (10.6 ml) while the temperature was kept at 0 – 5°C. The mixture was kept overnight at room temperature and it was then worked up in the usual manner giving 10.0 g of crude product. Crystallization from methanol gave 5.7 g (65 %) of (Xb), m.p. 90 – 93°C. Two additional recrystallizations gave the pure product, m.p. 93 – 95°C, $[\alpha]_D^{26} = -84.1°$ (*c* 1.4, $CHCl_3$). (Found: C 68.25; H 4.80. Calc. for $C_{27}H_{24}O_8$: C 68.07; H 5.08.)

Tri-O-*acetyl-2*-O-*methyl*-α-D-*xylopyranose* (*Xa*) was prepared as described by Robertson and Speedie.[10]

Reactions with hydrogen fluoride

Tri-O-*benzoyl-2*-O-*methyl*-α-D-*xylopyranose* (Xb) (2.0 g) was dissolved in hydrogen fluoride (4 ml) and kept at room temperature for 10 min. The solution was then worked up as described above and the crude product (1.51 g) was crystallized from ether – pentane yielding di-*O*-benzoyl-2-*O*-methyl-α-D-xylopyranosyl fluoride (α-XIIIb), 900 mg (57 %), m.p. 117 – 118°C. Recrystallization from the same solvents gave the pure product, m.p. 120 – 121°C, $[\alpha]_D^{23} = -56.7°$ (*c* 0.3, $CHCl_3$). (Found: C 64.37; H 5.11. Calc. for $C_{20}H_{19}O_6F$:

C 64.16; H 5.12.) The material in the mother liquors was separated into two fractions by preparative TLC (ether – pentane 1 : 1). The slow moving fraction gave 323 mg of pure (α-XIIIb), bringing the total yield of this compound to 78 %. The fast running fraction was a mixture of two compounds which were separated by preparative TLC using two elutions with benzene. The fastest running of these fractions gave 89 mg (6 %) of di-*O*-benzoyl-2-*O*-methyl-β-D-xylopyranosyl fluoride (β-XIIIb), which was crystallized from ether – pentane, m.p. 82 – 83°C, $[\alpha]_D^{22} = -133°$ (*c* 1.6, $CHCl_3$). (Found: C 64.15; H 5.02.) The slow moving fraction gave 26 mg (1.6 %) of di-*O*-benzoyl-2-*O*-methyl-α-D-xylofuranosyl fluoride identical with the product described below.

Treatment of (Xb) (1.0 g) with hydrogen fluoride for 170 h at 0 – 5° gave a dark coloured solution. Work up yielded 500 mg of crude product which was benzoylated with benzoyl chloride in pyridine. The product thus obtained was separated into two fractions by preparative TLC using benzene as eluent. The fastest moving fraction gave 269 mg (34 %) of di-*O*-benzoyl-2-*O*-methyl-α-D-xylofuranosyl fluoride (α-XII) as a colourless syrup, $[\alpha]_D^{25} = -32.5°$ (*c* 0.65; $CHCl_3$). (Found: C 64.16; H 4.83. Calc. for $C_{20}H_{19}O_6F$: C 64.16; H 5.12.) The slow moving fraction gave 100 mg (13 %) of impure di-*O*-benzoyl-2-*O*-methyl-β-D-xylofuranosyl fluoride (β-XII). Attempts to obtain the pure product by preparative TLC were unsuccessful. The NMR spectrum of the product, which contained *ca.* 15 % of an unidentified impurity, was well resolved (Table 2) and proved the structure.

When (Xb) was treated with hydrogen fluoride for 20 h at room temperature and worked up as described above 27 % of pure (α-XII) and 11 % of impure (β-XII) was obtained.

Microanalyses were performed by Dr. A. Bernhardt.

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