Reactions of Acylated Pentoses and Acylated Methyl Pentosides with Dibromomethyl Methyl Ether. Preparation of Bromo-deoxy-pentoses

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When acylated pentoses or acylated methyl pentosides are treated with dibromomethyl methyl ether and zinc bromide, acylated pentopyranosyl bromides are formed rapidly. In a further, slow reaction the pyranosyl bromides are converted into bromo-deoxy-pentosyl bromides, mostly with the bromo-substituent at C-2. Acetylated D-xylo-, D-arabino, and D-lyxo-pyranosyl bromides all yield 3,4-di-*O*-acetyl-2-bromo-2-deoxy-D-xylopyranosyl bromide, whereas tri-*O*-acetyl-D-ribopyranosyl bromide forms 3,4-di-*O*-acetyl-2-bromo-2-deoxy-D-arabino-pyranosyl bromide. The yields of 2-bromo-2-deoxy-products are low in the acetate series, but treatment of tri-*O*-benzoyl-D-xylopyranosyl bromide with dibromomethyl methyl ether gives a high yield of 2-bromo-2-deoxy-D-xylose derivatives.

Szabó *et al.*[1] have found that dibromomethyl methyl ether is a convenient reagent for the preparation of glycosyl bromides from acetylated carbohydrates or from acetylated glycosides. They prepared glycosyl bromides by treating an acylated sugar or glycoside with the dibromo-ether in boiling chloroform in the presence of zinc chloride. We used this reaction to prepare certain glycosyl bromides and observed that, when the reaction mixture was kept at room temperature or at +5° the initially formed glycosyl bromide underwent bromination to give dibromo-derivatives. This further reaction is slow; in boiling chloroform, which the Hungarian workers used,[1] the dibromomethyl methyl ether decomposes before it reacts with the initially formed bromides.

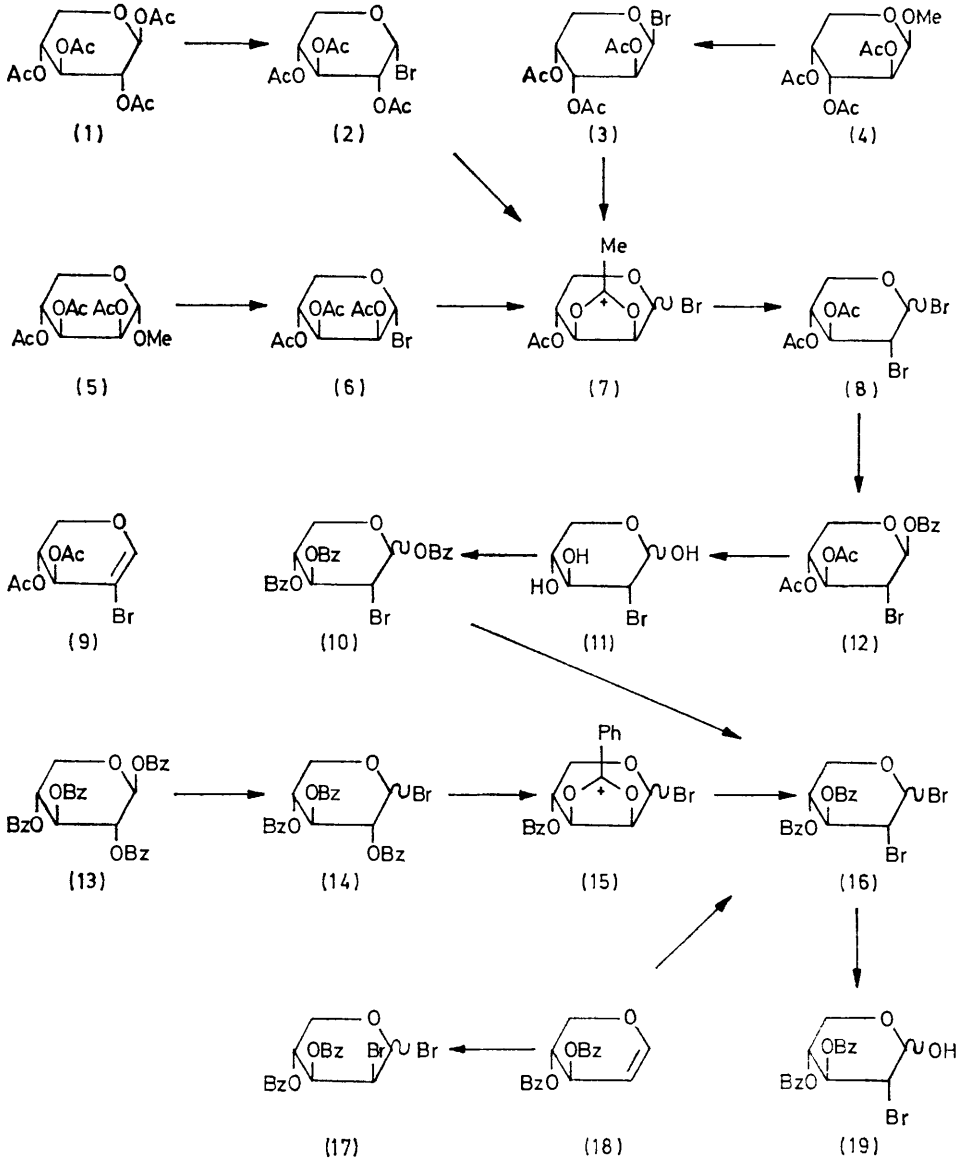
[1] J. F. Szabó, J. Farkas, R. Bognár, and H. Gross, *Acta Chim. Acad. Sci. Hung.*, 1970, **64**, 67.

When tetra-*O*-acetyl-β-D-xylopyranose (1) was treated with dibromomethyl methyl ether and zinc bromide in chloroform at room temperature for 10 min, tri-*O*-acetyl-α-D-xylopyranosyl bromide (2) was formed in good yield. If the mixture was kept at +5° a further reaction took place, as seen from n.m.r. spectra, and after *ca.* 1 week the bromide (2) had disappeared completely. Work-up gave a crude syrup which probably contained 3,4-di-*O*-acetyl-2-bromo-2-deoxy-D-xylopyranosyl bromide (8). The product was unstable and it was therefore treated immediately with silver benzoate in acetonitrile. This gave 3,4,di-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-β-D-xylopyranose (12), which was isolated in 33% yield. A small amount of 3,4-di-*O*-acetyl-2-bromo-1,2-dideoxy-D-*threo*-pent-1-enopyranose (9) was also obtained, probably formed by elimination of hydrogen bromide from the dibromo-compound (8).

Similar treatment of methyl tri-*O*-acetyl-β-D-arabinopyranoside (4) with the dibromo-ether and zinc bromide gave the tri-*O*-acetyl-β-D-arabinopyranosyl bromide (3).[2] This also reacted further with the dibromo-ether: after 6 days at +5° its n.m.r. signals were not detectable in the spectrum of the reaction mixture. Work-up and treatment of the crude product with silver benzoate gave a 29% yield of the 2-bromo-derivative (12) and small amounts of the unsaturated sugar (9).

Reaction of methyl tri-*O*-acetyl-α-D-lyxopyranoside (5) with the dibromo-ether gave tri-*O*-acetyl-α-D-lyxopyranosyl bromide (6), as seen from an n.m.r. spectrum. The latter was also converted into the dibromo-compound (8) by further reaction, and the 1-*O*-benzoate (12) was isolated in 20% yield after treatment with silver benzoate

Thus the acetylated xylo-, arabino-, and lyxo-pyranosyl bromides all gave the same product (8) on treatment



[2] K. Bock and C. Pedersen, in preparation.

with dibromomethyl methyl ether. The yields were low, probably owing to decomposition of (8), but no other products were detected in appreciable amounts.

Finally, tetra-*O*-acetyl-β-D-ribopyranose (20) was treated with the dibromo-ether and zinc bromide. The β-bromide (21) was formed rapidly and on further reaction it disappeared. After 48 h at +20° the mixture was worked up and the product was treated with silver benzoate. This gave a 14% yield of 3,4-di-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-α-D-arabinopyranose (22). A small amount of the 4-bromo-compound (23) was also isolated.

Since the yields were low in all the foregoing reactions we then studied the corresponding benzoates, as these would be expected to give more stable products. Treatment of tetra-*O*-benzoyl-β-D-xylopyranose (13) with the dibromo-ether and zinc bromide for 20 min gave a good yield of tri-*O*-benzoyl-α-D-xylopyranosyl bromide (14α). Further reaction for 24 h at room temperature led to a mixture of the anomeric 3,4-di-*O*-benzoyl-2-bromo-2-deoxy-D-xylopyranosyl bromides (16). Fractional crystallization of this mixture gave the pure α- and β-anomers. In other experiments the crude product was hydrolysed. This gave crystalline 3,4-di-*O*-benzoyl-2-bromo-2-deoxy-D-xylopyranose (19) in 80% yield, and this reaction therefore provides a convenient method for the preparation of 2-bromo-2-deoxy-D-xylose derivatives.

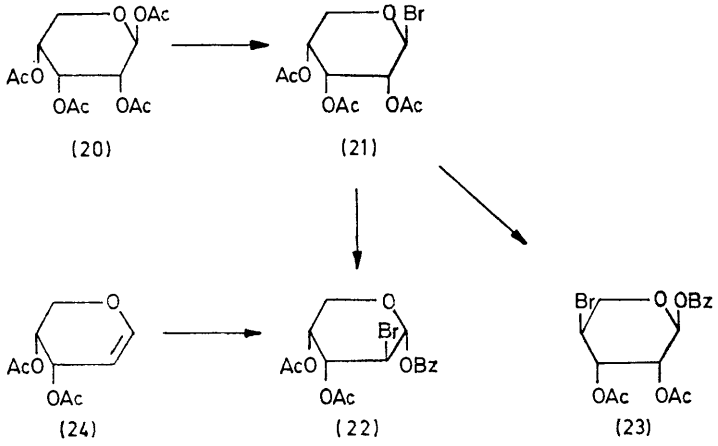
The tribenzoates of arabino-, lyxo-, and ribo-pyranosyl bromide did not react with the dibromo-ether and zinc bromide.

The 2-bromo-2-deoxy-compounds (12), (16), and (19) were identified primarily from the n.m.r. spectra (Table) which are all well resolved. In order to confirm the structures, 3,4-di-*O*-benzoyl-1,2-dideoxy-D-*threo*-pent-1-enopyranose (18) was treated with bromine. This gave a 33% yield of the glycosyl bromide (16β) and 7% of the corresponding α-anomer, both identical with those obtained by reaction of (14) with the dibromo-ether. In addition, the bromination of (18) gave the epimeric products (17) with the D-*lyxo*-configuration. The reaction does not provide an unambiguous proof of the structure of (16). It does, however, prove the configuration at C-3 and C-4, and it shows that the bromo-substituent is at C-2.

The acetate (12) was hydrolysed to 2-bromo-2-deoxy-D-xylose (11), which was benzoylated to give the tribenzoate (10). Treatment of the latter with the dibromo-ether followed by hydrolysis gave the 1-hydroxy-compound (19).

Treatment of 3,4-di-*O*-acetyl-1,2-dideoxy-D-*erythro*-pent-1-enopyranose (24) with bromine, followed by reaction with silver benzoate, gave, among other products, the bromo-benzoate (22), identical with the compound obtained from tetra-*O*-acetyl-β-D-ribopyranose (20) by reaction with the dibromo-ether. Thus the configuration at C-3 and C-4 of (22) is established and the n.m.r. data (Table) are consistent only with the proposed structure.

The fact that the triacetates of xylo, lyxo-, and arabino-pyranosyl bromide all gave the 2-bromo-D-xylose derivative (12) on treatment with the dibromo-ether suggests that the acetoxonium ion (7) is an intermediate in this



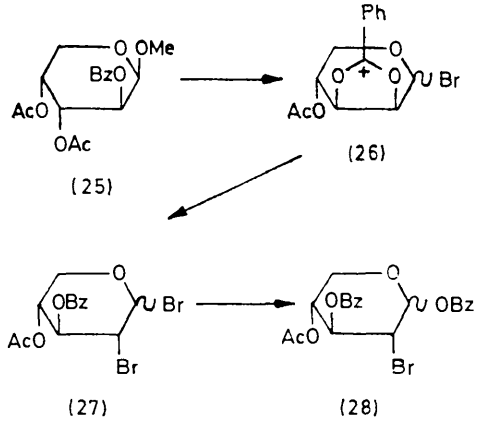
reaction. The ion (7) could be formed from the glycosyl bromides (2), (3), and (6) by inversion at not more than one carbon atom. The tri-*O*-acetyl-D-ribopyranosyl bromide (21) would, on the other hand, not be expected to form the ion (7); in fact it does not yield (12) on treatment with the dibromo-ether.

According to the mechanism proposed by Szabó *et al.*,[1] attack of the cation $[BrCH \cdots OMe]^+$ on an acetylated sugar could result in loss of an *O*-acetyl group. The acetoxonium ion (7) could then arise from the xylosyl bromide (2) by loss of the *O*-acetyl group at C-2 with anchimeric assistance from the acetoxy-group at C-3. Analogously, the arabinosyl bromide (3) could form the ion (7) by loss of the acetoxy-group at C-3. Subsequent attack of a bromide ion at C-2 of the acetoxonium ion (7) would result in *trans*-opening and formation of compound (8). Attack of bromide on C-2 would yield a 3-bromo-3-deoxy-D-arabinose derivative. Such a product was, however, not found, presumably because the acetoxonium ion (7) is opened by migration of bromine from C-1 to C-2 and not by attack of bromide ions from the solution. This would be analogous to the observation [3] of

[3] H. J. Jennings, *Canad. J. Chem.*, 1970, **48**, 1834.

migration of a chloro-substituent from C-1 to C-2 when chlorosulphates of xylo- and lyxo-pyranosyl chlorides were treated with aluminium chloride.

If the foregoing mechanism is correct, a benzoxonium ion (15) should be an intermediate in the conversion of tri-*O*-benzoyl-D-xylopyranosyl bromide (14) into the bromo-deoxy-sugar (16). That dioxolanylium ions are probably intermediates in these reactions was shown by treating methyl 3,4-di-*O*-acetyl-2-*O*-benzoyl-β-D-arabinopyranoside (25) with the dibromo-ether and zinc bromide. This gave the 4-*O*-acetyl-3-*O*-benzoyl-2-bromo-2-deoxy-D-xylopyranosyl bromides (27), isolated as the 1-*O*-benzoates (28). In this reaction the benzoyl group has migrated from C-2 to C-3 while the stereochemistry at both carbon atoms is inverted, and this suggests strongly that the benzoxonium ion (26) is an intermediate.



The use of several catalysts other than zinc bromide was investigated. When tetra-*O*-benzoyl-β-D-xylopyranose (13) was treated with the dibromo-ether in the presence of mercuric chloride or aluminium chloride, tri-*O*-benzoyl-α- and β-D-xylopyranosyl bromide were formed, but 2-bromo-2-deoxy-compounds were not obtained by further reaction. Treatment of compound (13) with the dibromo-ether in the presence of boron trifluoride gave a good yield of the previously unknown tri-*O*-benzoyl-β-D-xylopyranosyl bromide (14β). With zinc bromide the more stable α-bromide was obtained.

N.m.r. spectra of bromo-deoxy-pentoses *

Compd.	Solvent	δ Values H-1	H-2	H-3	H-4	H-5*eq*	H-5*ax*	Coupling constants (Hz) $J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5eq}$	$J_{4,5ax}$	$J_{5,5}$		Predominant conformation
(12)	$CDCl_3$	6·08	4·08	5·45	5·01	4·22	3·64	8·2	9·6	8·4	5·2	9·5	11·6		$^4C_1$
(16α)	$CDCl_3$	6·52	4·33	6·09	5·38	4·34	4·23	3·3	10·4	9·4	6·0	10·2	11·0		$^4C_1$
(16β)	$CDCl_3$	6·75	4·74	5·72	5·28	4·16	4·64	*ca.* 1	2·6	1·8	2·0	2·3	12·8	$\{J_{3,5eq}$ 1·8, $J_{1,5ax}$ *ca.* 0·5$\}$	$^1C_4$
(19α)	$(CD_3)_2CO$	5·50	4·41	6·08	5·32	4·02	4·18	3·0	10·5	8·9	6·6	9·7	10·7		$^4C_1$
(19β)	$(CD_3)_2CO$	5·13	4·15	5·85	5·27	4·31	3·76	8·3	10·3	9·1	4·9	10·4	11·6		$^4C_1$
(14β)	$CDCl_3$	6·60	5·55—5·70		5·29	4·19	4·65	<1		*ca.* 1	1·7	2·0	13·2	$\{J_{3,5eq}$, *ca.* 1 $J_{1,5eq}$ <1$\}$	$^1C_4$
(22)	C_6D_6	6·03	4·33	5·10—5·30		3·62	3·13	8·3	9·8	3·4	2·5	1·4	13·0		$^1C_4$
(17α)	$CDCl_3$	6·67	5·03	5·98	5·86	4·35	4·09	1·4	3·5	10·0	5·4	10·0	11·0	$J_{1,5ax}$ *ca.* 0·5	$^4C_1$
(17β)	$CDCl_3$	6·52	4·88	5·66	5·29	4·08	4·57	3·9	3·9	3·5	1·6	1·4	13·0	$\{J_{1,3}$ *ca.* 0·5, $J_{1,4}$ *ca.* 0·5 $J_{1,5ax}$ *ca.* 0·5, $J_{3,5eq}$ 1·6$\}$	$^1C_4$
(23)	C_6D_6	6·34	5·45	5·60	4·21	3·77	3·94	2·2	3·4	10·2	6·1	10·2	11·6		$^1C_4$(L)
(9)	$CDCl_3$	6·88		5·33	4·99	4·28	3·93			1·6	2·6	1·6	12·0	$\{J_{1,3}$ 0·5 $J_{1,5ax}$ *ca.* 0·3. $J_{3,5eq}$ 1·6$\}$	$^5H_1$
(27α)	$CDCl_3$	6·48	4·24	5·96	5·22	3·9—4·3		3·5	9·5	10·5					$^4C_1$
(28β)	$CDCl_3$	6·20	4·28	5·73	5·19	4·30	3·76	7·6	9·5	8·8	5·0	9·0	12·0		$^4C_1$
(25)	$CDCl_3$	5·11	5·41	5·60	5·40	3·97	3·73	3·5	10·5	3·1	1·3	1·8	13·0	$J_{1,5eq}$ 0·4	$^1C_4$

* The assignments were confirmed by spin-decoupling or INDOR experiments at 100 MHz.

Dichloromethyl methyl ether reacts with acetylated carbohydrates in the presence of zinc chloride to give acetochloro-compounds.[1,4] In view of the foregoing results it might be expected that prolonged reaction with the dichloro-ether would lead to 2-chloro-2-deoxy-compounds. This was, however, not the case. Thus treatment of tetra-*O*-acetyl-β-D-xylopyranose (1) with dichloromethyl methyl ether and zinc chloride gave tri-*O*-acetyl-α-D-xylopyranosyl chloride as the final product. Analogous results were obtained with the tetrabenzoate (13).

EXPERIMENTAL

Preparative t.l.c. was performed on 1 mm layers of silica gel (Merck PF_{254}). Solvents were evaporated off *in vacuo* at 20°. N.m.r. spectra were measured on Varian A-60 and HA-100 instruments with tetramethylsilane as internal reference. Optical rotations were measured for solutions in chloroform.

Tri-O-acetyl-α-D-xylopyranosyl Bromide (2).—To tetra-*O*-acetyl-β-D-xylopyranose (1) (1·0 g) in chloroform (1·5 ml), dibromomethyl methyl ether (0·5 ml) and zinc bromide (130 mg) were added, and the mixture was stirred for 10 min at room temperature. It was then diluted with dichloromethane and washed with 4N-hydrochloric acid until it was clear (3—5 times). It was subsequently washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The residue crystallized from ether-pentane to give the product (2) (840 mg, 78%), m.p. 94—96°. An additional recrystallization gave a product with m.p. 96—97°, $[\alpha]_D^{23}$ +207° (*c* 2·0) (lit.,[5] m.p. 102°, $[\alpha]_D^{20}$ +212°). An

[4] H. Gross and I. Farkas, *Chem. Ber.*, 1960, **93**, 95.
[5] J. K. Dale, *J. Amer. Chem. Soc.*, 1915, **37**, 2745.

n.m.r. spectrum was identical with that previously described.[6]

Tri-*O*-acetyl-β-D-ribopyranosyl bromide (21) was prepared similarly, in 70% yield, from the tetra-acetate (20). Crystallization of the crude product twice from ether–pentane gave material of m.p. 94—95°, $[\alpha]_D^{24}$ −218° (*c* 2·8) (lit.,[7] m.p. 96°, $[\alpha]_D$ −209°). An n.m.r. spectrum confirmed the structure.[6]

Tri-O-*benzoyl*-α-D-*xylopyranosyl Bromide* (14α).—To a solution of the tetrabenzoate (13) (1·28 g) in chloroform (1·5 ml), dibromomethyl methyl ether (1·0 ml) and anhydrous zinc bromide (250 mg) were added, and the mixture was stirred for 20 min at room temperature. Work-up as before and crystallizations from ether–pentane gave a product (917 mg, 78%) with m.p. 116—122°, $[\alpha]_D^{21}$ +77·5° (*c* 1·7). An n.m.r. spectrum indicated that this was a mixture of the anomeric bromides (14), in α : β ratio 10 : 1. Four recrystallizations from benzene–pentane gave pure (14α), m.p. 134—135°, $[\alpha]_D^{21}$ +116° (*c* 1·0). These values are in good agreement with those reported,[8,9] and the n.m.r. spectrum confirmed the structure.

Tri-O-*benzoyl*-β-D-*xylopyranosyl Bromide* (14β).—To a solution of the tetrabenzoate (13) (1·16 g) in chloroform (1·5 ml), the dibromo-ether (0·5 ml) and boron trifluoride–ether complex (0·1 ml) were added, and the mixture was kept at room temperature for 3 h. It was then diluted with dichloromethane (50 ml), washed with aqueous sodium hydrogen carbonate, dried, and evaporated at 20°. The residue crystallized from ether–pentane to give the *product* (14β) (874 mg, 74%), m.p. 133—136°, $[\alpha]_D^{22}$ −135° (*c* 1·0). Four recrystallizations from benzene–pentane gave the pure product, m.p. 146—147°, $[\alpha]_D^{22}$ −143° (*c* 1·0); for n.m.r. see Table (Found: C, 59·35; H, 4·0; Br, 15·1. $C_{26}H_{21}BrO_7$ requires C, 59·45; H, 4·05; Br, 15·2%).

3,4-*Di*-O-*acetyl*-1-O-*benzoyl*-2-*bromo*-2-*deoxy*-β-D-*xylopyranose* (12).—(*a*) Tetra-*O*-acetyl-β-D-xylopyranose (1) (506 mg) was dissolved in chloroform (1·5 ml) and anhydrous zinc bromide (193 mg) was added. The mixture was stirred at +5° for 7 days and 1 ml of the dibromo-ether was added every day (total 6 ml). The mixture was then worked up as before and the crude product was dissolved in acetonitrile (30 ml) and stirred with silver benzoate (2·0 g) for 8 h at room temperature. The mixture was filtered through activated carbon and evaporated. The residue was dissolved in dichloromethane and washed with aqueous sodium hydrogen carbonate. The solution was dried and evaporated leaving a syrup (413 mg), which was separated into two fractions by preparative t.l.c. with ether–pentane (1 : 1) as eluant. The faster running fraction gave a syrup (30 mg, 7%) which was not investigated further. Its n.m.r. spectrum (Table) indicated that it was 3,4-di-*O*-acetyl-2-bromo-1,2-dideoxy-D-*threo*-pent-1-enopyranose (9). The slower running fraction gave the *product* (12) (207 mg, 33%) m.p. 115—116°, $[\alpha]_D^{20}$ −23·5° (*c* 1·5). Two recrystallizations from ether–pentane gave the pure product, m.p. 120—121°, $[\alpha]_D^{20}$ −25·0° (*c* 1·8) (Found: C, 48·0; H, 4·4; Br, 20·05. $C_{16}H_{17}BrO_7$ requires C, 47·9; H, 4·3; Br, 19·9%).

(*b*) Methyl tri-*O*-acetyl-β-D-arabinopyranoside (4) (554 mg) in chloroform (1 ml) was treated with zinc bromide (174 mg) and the dibromo-ether (4 × 1 ml) at +5° for 6 days. The crude product was then treated with silver benzoate and chromatographed as in (*a*). This gave the 2-bromo-xylal (9) (40 mg, 7·5%), identified through its n.m.r. spectrum only. The main fraction yielded compound (12) (225 mg, 29%), m.p. 112—115°, $[\alpha]_D^{20}$ −24·4° (*c* 1·5).

In addition, a slow-running fraction gave 2,3,4-tri-*O*-acetyl-1-*O*-benzoyl-α-D-arabinopyranose (85 mg, 12%), m.p. 147—148° (from ether–pentane), $[\alpha]_D^{20}$ +11·9° (*c* 3·7) (lit.,[10] m.p. 149—150°, $[\alpha]_D$ +11·9°). The n.m.r. spectrum agreed with the structure.

(*c*) Methyl tri-*O*-acetyl-α-D-lyxopyranoside (5) (955 mg) in chloroform (2 ml) was treated with zinc bromide (218 mg) and the dibromo-ether (4 × 1 ml) at +5° for 10 days. Further treatment as in (*a*) gave compounds (9) (73 mg, 8%) and (12) (261 mg, 20%), m.p. 114—116°, $[\alpha]_D^{21}$ +25·9° (*c* 1·7).

Reaction of Tetra-O-*acetyl*-β-D-*ribopyranose with the Dibromo-ether.*—The tetra-acetate (20) (724 mg) in chloroform (0·5 ml) was treated with zinc bromide (140 mg) and the dibromo-ether (3 × 1 ml) at room temperature for 48 h. Work-up as before followed by treatment with silver benzoate gave a crude product (548 mg) which was separated into three fractions by preparative t.l.c. [ether–pentane (1 : 1) as eluant].

The fastest moving fraction was rechromatographed and the product crystallized from ether–pentane to give 2,3-*di*-O-*acetyl*-1-O-*benzoyl*-4-*bromo*-4-*deoxy*-α-L-*lyxopyranose* (23) (30 mg, 3·3%), m.p. 149—150°, $[\alpha]_D^{20}$ −54·0° (*c* 1·2). Two additional recrystallizations gave a product of m.p. 149—150°, $[\alpha]_D^{20}$ −60·5° (*c* 1·0) (Found: C, 47·85; H, 4·4. $C_{16}H_{17}BrO_7$ requires C, 47·9; H, 4·3%). The structure was determined from the n.m.r. spectrum only (Table). The high-field position of the signal of H-4 shows that the bromine is at C-4, and, unless the configurations of both C-2 and C-3 were inverted in the reaction, the coupling constants are only compatible with an L-*lyxo*-configuration.

The next fraction gave 3,4-di-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-α-D-arabinopyranose (22) (124 mg, 14%), m.p. 143—144° (from ether–pentane), $[\alpha]_D^{21}$ −4·47 (*c* 2·0), identical (n.m.r. spectrum) with the product described later.

A slower running fraction gave 2,3,4-tri-*O*-acetyl-1-*O*-benzoyl-α-D-ribopyranose (113 mg, 13%), which could not be induced to crystallize. An n.m.r. spectrum was identical with that described.[8]

3,4-*Di*-O-*benzoyl*-2-*bromo*-2-*deoxy*-D-*xylopyranosyl Bromides* (16).—Tri-*O*-benzoyl-α-D-xylopyranosyl bromide (5·07 g) in chloroform (20 ml) was stirred with the dibromo-ether (7 ml) and zinc bromide (430 mg) for 24 h at room temperature. More dibromo-ether (3 ml) was then added and the mixture was stirred for 24 h. Work-up as before gave crude product (4·93 g), which was dissolved in ether and kept overnight at +5°. The crystalline product was filtered off (fraction 1) and the mother liquor was diluted with pentane (50 ml) and cooled overnight to give a second batch (fraction 2). The mother liquor was then evaporated and the residue was crystallized from ether–pentane (1 : 5; 100 ml) to give fraction 3.

Fraction 1 (709 mg, 15%), m.p. 132—135°, $[\alpha]_D^{20}$ −144° (*c* 1), was recrystallized three times from benzene–pentane to give 3,4-*di*-O-*benzoyl*-2-*bromo*-2-*deoxy*-β-D-*xylopyranosyl bromide* (16β), m.p. 141—142°, $[\alpha]_D^{20}$ −168° (*c* 1·0) (Found: C, 47·05; H, 3·2; Br, 33·05. $C_{19}H_{16}Br_2O_5$ requires C, 47·15; H, 3·35; Br, 33·0%).

[6] P. L. Durette and D. Horton, *Carbohydrate Res.*, 1971, **18**, 57.
[7] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, 1931, **92**, 109.
[8] P. L. Durette and D. Horton, *Carbohydrate Res.*, 1971, **18**, 389.
[9] H. G. Fletcher, jun., and C. S. Hudson, *J. Amer. Chem. Soc.*, 1950, **72**, 4173.
[10] K. Bock and C. Pedersen, *Acta Chem. Scand.*, 1970, **24**, 2465.

Fraction 2 (0·464 g, 10%) consisted of a mixture of (16α) and (16β) in a 3 : 2 ratio as seen from an n.m.r. spectrum.

Fraction 3 (1·65 g, 35%), m.p. 110—112°, $[\alpha]_D^{20}$ +106·3° (*c* 1·6) was recrystallized three times from ether–pentane to give pure α-*anomer* (16α), m.p. 120—121°, $[\alpha]_D^{20}$ +121·5° (Found: C, 47·05; H, 3·3; Br, 33·2%).

3,4-*Di*-O-*benzoyl*-2-*bromo*-2-*deoxy*-D-*xylopyranose* (19).—Treatment of compound (14α) (5·0 g) with the dibromo-ether as before gave a crude product (5·4 g). This was dissolved in acetone (200 ml) and water (30 ml) and lead carbonate (10 g) was added. The mixture was stirred for 15 h, the lead salts were filtered off, and the solution was evaporated. The residue was dissolved in dichloromethane; the solution was filtered and evaporated to give a crystalline product (4·78 g). This was extracted with ether (75 ml); the solution was filtered and evaporated and the residue was again extracted with ether (50 ml). Evaporation gave a product which did not contain lead salts. Recrystallization from ether–pentane gave *compound* (19) (3·20 g, 80%), m.p. 138—141°, $[\alpha]_D^{20}$ −46·0° (2 min) ⟶ −30·5° (48 h) (*c* 2·6). Two additional recrystallizations gave a product with m.p. 145—146°, $[\alpha]_D^{20}$ −64·5° (2 min) ⟶ −30·8° (48 h) (*c* 2·5° (Found: C, 54·3; H, 4·2; Br, 18·8. $C_{19}H_{17}BrO_6$ requires C, 54·15; H, 4·05; Br, 18·95%). The n.m.r. data for the two anomers (Table) were obtained from the mixture after mutarotation had ceased.

Reaction of 3,4-*Di*-O-*benzoyl*-1,2-*dideoxy*-D-threo-*pent*-1-*enopyranose* (18) *with Bromine*.—To a solution of compound (18) (1·02 g) in benzene (20 ml) was added bromine (0·16 ml) in benzene (10 ml). After 30 min at room temperature the solvent was evaporated off and the residue (1·72 g) was crystallized from ether–pentane to give 3,4-di-*O*-benzoyl-2-bromo-2-deoxy-β-D-xylopyranosyl bromide (16β) (498 mg, 33%), m.p. 129—131°. Recrystallization gave the pure product, m.p. 135—137°, $[\alpha]_D^{20}$ −172° (*c* 2·5), identical (n.m.r. spectrum) with the material already described.

Crystallization of the material in the mother liquors from ether–pentane gave 3,4-*di*-O-*benzoyl*-2-*bromo*-2-*deoxy*-β-D-*lyxopyranosyl bromide* (17β) (178 mg, 12%), m.p. 133—139°, $[\alpha]_D^{20}$ −202° (*c* 1·4). Two recrystallizations from ether–pentane gave the pure product, m.p. 143—144°, $[\alpha]_D^{21}$ −234° (*c* 1·5) (Found: C, 47·05; H, 3·2; Br, 32·75. $C_{19}H_{16}Br_2O_5$ requires C, 47·15; H, 3·35; Br, 33·0%).

The material in the combined mother liquors was then separated into three fractions by preparative t.l.c. with ether–pentane (1 : 3) as eluant. The fastest moving fraction gave 3,4-*di*-O-*benzoyl*-2-*bromo*-2-*deoxy*-α-D-*lyxopyranosyl bromide* (17α) (181 mg, 8%), m.p. 135—137°, $[\alpha]_D^{21}$ + 32·0° (*c* 2·0). Two recrystallizations from ether–pentane gave the pure product, m.p. 144—145°, $[\alpha]_D^{22}$ +36·3° (*c* 1·6) (Found: C, 47·25; H, 3·45; Br, 33·0%).

The next fraction yielded (16α) (113 mg, 7·5%), which was recrystallized twice from ether–pentane; m.p. 114—115°, $[\alpha]_D^{21}$ +110·0° (*c* 2·0).

The slowest moving fraction gave 3,4-di-*O*-benzoyl-2-bromo-2-deoxy-D-xylopyranose (19) (132 mg, 10%), m.p. 145—146° (from ether–pentane), $[\alpha]_D^{20}$ −47·7° ⟶ −31·8° (4 days) (*c* 2·7).

Reaction of 3,4-*Di*-O-*acetyl*-1,2-*dideoxy*-D-erythro-*pent*-1-*enopyranose* (24) *with Bromine*.—A solution of compound (24) (0·843 g) in benzene (30 ml) was treated with a slight excess of bromine for 5 min at 10°. Silver benzoate (1·8 g) was then added and the mixture was stirred for 30 min at room temperature. Filtration through activated carbon and evaporation gave a crude product which was separated into several fractions by preparative t.l.c. The main fraction crystallized from ether–pentane to give 3,4-*di*-O-*acetyl*-1-O-*benzoyl*-2-*bromo*-2-*deoxy*-α-D-*arabinopyranose* (22) (578 mg, 34%), m.p. 143—144°, $[\alpha]_D^{22}$ −7·8° (*c* 2·0). Two additional recrystallizations gave pure (22), m.p. 144—145°, $[\alpha]_D^{20}$ −5·3° (*c* 2·0) (Found: C, 48·05; H, 4·4; Br, 19·85. $C_{16}H_{17}BrO_7$ requires C, 47·9; H, 4·3; Br, 19·9%).

Conversion of 3,4-*Di*-O-*acetyl*-1-O-*benzoyl*-2-*bromo*-2-*deoxy*-β-D-*xylopyranose* (12) *into Compound* (19).—A solution of compound (12) (217 mg) in 0·1N-hydrochloric acid (15 ml) was boiled for 4 h. It was then neutralized with Amberlite IR-4B resin and evaporated to dryness. Pyridine was added and evaporated off to remove the last traces of water, and the residue was benzoylated with benzoyl chloride (3 ml) in pyridine (10 ml). The product was purified by preparative t.l.c. [ether–pentane (1 : 1)] to give a syrup (103 mg), which was a mixture of the anomeric tri-*O*-benzoyl-2-bromo-2-deoxy-D-xylopyranoses (10) as seen from an n.m.r. spectrum.

This product was converted into the glycosyl bromide (16) by brief treatment with the dibromo-ether and zinc bromide (see before). Subsequent hydrolysis with aqueous acetone as before gave compound (19) (65 mg), m.p. 143—144° (from ether–pentane), $[\alpha]_D^{26}$ −47·4 ⟶ −31·5° (3 days) (*c* 1·0), identical (n.m.r. spectrum) with that already described.

Methyl 3,4-*Di*-O-*acetyl*-2-O-*benzoyl*-β-D-*arabinopyranoside* (25).—Methyl 2-*O*-benzoyl-β-D-arabinopyranoside [11] (1·50 g) was acetylated with acetic anhydride (5·0 ml) in pyridine (10 ml). The product (1·88 g, 90%) was purified by preparative t.l.c. with ether–pentane (1 : 1) as eluant. The pure *product* was a syrup, $[\alpha]_D^{22}$ −166° (*c* 2·0) (Found: C, 58·3; H, 5·4. $C_{17}H_{20}O_8$ requires C, 58·0; H, 5·7%); for n.m.r. data see Table.

Reaction of Compound (25) *with Dibromomethyl Methyl Ether*.—A mixture of compound (25) (587 mg), chloroform (3 ml), the dibromo-ether (1 ml), and zinc bromide (200 mg) was stirred for 16 h at room temperature. More dibromo-ether (1 ml) was then added and the mixture was stirred for 8 h. Work-up as before gave a crude product (750 mg), which, as seen from an n.m.r. spectrum, consisted mainly of a mixture of the anomeric 4-*O*-acetyl-3-*O*-benzoyl-2-bromo-2-deoxy-D-xylopyranosyl bromides (27) (n.m.r. data for the α-anomer are shown in the Table).

This product was treated with silver benzoate (2·0 g) in acetonitrile (20 ml) as before and the material thus obtained (680 mg) was separated into two fractions by preparative t.l.c. with ether–pentane (1 : 1) as eluant. The fastest moving fraction gave 4-*O*-acetyl-3-*O*-benzoyl-2-bromo-1,2-dideoxy-D-*threo*-pent-1-enopyranose (86 mg, 15%), which was only characterized by its n.m.r. spectrum.

The next fraction gave 4-*O*-acetyl-1,3-di-*O*-benzoyl-2-deoxy-2-bromo-D-xylopyranose (28) (290 mg, 35%) as a mixture of anomers (α : β ratio 1 : 3) which was difficult to separate. Two chromatographic separations using ether–pentane (1 : 2) and ether–pentane (2 : 1) gave the β-*anomer* (28β) (60 mg), m.p. 65—68° (decomp.) (from ether–pentane), $[\alpha]_D^{21}$ +20·5 (*c* 0·665) (Found: C, 54·25; H, 4·2; Br, 17·7. $C_{21}H_{19}BrO_7$ requires C, 54·45; H, 4·15; Br, 17·25%). Besides the n.m.r. spectral data shown in the Table, signals corresponding to one acetyl group and two benzoyl groups were present. That the *O*-benzoyl group of (28β) is at C-3 is seen from the H-3 signal, which is shifted 0·3 p.p.m. downfield compared to H-3 of (12).

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[11] M. A. Oldham and J. Honeyman, *J. Chem. Soc.*, 1946, 986.