Carbohydrate Research, (1991) 171–178
Elsevier Science Publishers B.V., Amsterdam

A new type of anhydro sugar: 1,3^1-anhydro-3-*C*-hydroxymethylaldoses*,†

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(Received November 27th, 1990; accepted for publication, January 17th, 1991)

ABSTRACT

3-*C*-Hydroxymethyl-D-glucose, when heated with dilute acids, rapidly forms 96% of the 1,3^1-anhydride. 3-*C*-Hydroxymethyl-D-xylose, -L-lyxose, and -D-ribose each form an equilibrium that contains similar anhydrides but to a progressively lesser extent. Each of these branched-chain sugars has six cyclic forms in aqueous solution and their proportions have been determined.

INTRODUCTION

It is well known[2] that aldoses which have a hydroxymethyl group attached to C-5 are converted into 1,6-anhydrides on being heated with acids in aqueous solution. The extent of anhydride formation varies widely, according to the configuration of the sugar and the anhydride. A hydroxymethyl group attached to C-3 in a branched-chain sugar is in the same geometrical arrangement as one attached to C-5, and should give rise to a 1,3^1-anhydride.

Several 3-*C*-hydroxymethyl and 3-deoxy-3-*C*-hydroxymethyl sugars occur in Nature or have been synthesised. In particular, Dahlman *et al.*[3] have synthesised 3-*C*-hydroxymethyl-D-xylose, -D-ribose, and -L-lyxose, and the last one proved to be identical with a sugar isolated from a lipopolysaccharide. It is now shown that such branched-chain sugars form 1,3^1-anhydrides as readily as, and for some compounds more readily than, aldohexoses form 1,6-anhydrides.

RESULTS AND DISCUSSION

In order to study the existence and behaviour of 1,3^1-anhydrides, the preparation of the anhydride of 3-*C*-hydroxymethyl-D-glucose was attempted. This sugar has not been described hitherto, but its 1,2:5,6-di-*O*-isopropylidene derivative is known[3]. Heating this derivative with dilute sulfuric acid, or keeping a solution in aq. 75% trifluoroacetic acid at ambient temperature for several days, produced a crystalline compound as the main product. The ^{1}H-n.m.r. spectrum left no doubt that this product was 1,3^1-anhydro-3-*C*-hydroxymethyl-α-D-glucopyranose (**1**); in particular, the low $J_{1,2}$ value

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* Dedicated to Professor Grant Buchanan on the occasion of his 65th birthday.

† Conformational Analysis in Carbohydrate Chemistry, Part VI. For Part V, see ref. 1.

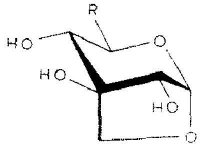
(~ 0.5 Hz) and the long-range coupling ($J_{4,3'_{exo}}$ 1.75 Hz) is characteristic and is encountered in the 1,6-anhydroaldose series[4,5]. The anhydride gave a crystalline tetra-acetate that had essentially the same *J* values and for which signals of H-2,4 had moved markedly downfield, but not that of H-1.

It proved to be more difficult to obtain the free sugar. Even mild methods for removing the isopropylidene groups produced a mixture of the sugar and its anhydride. Clearly, the anhydride is formed very readily. Very mild methods of hydrolysis (*e.g.*, aq. 50% acetic acid at ambient temperature) hydrolysed the intermediate 1,2-acetal very slowly so that, by the time it was hydrolysed, some anhydride was present. The sugar is readily separated from the two other compounds by column chromatography on silica gel. The method ultimately adopted involved aq. 2.0% trifluoroacetic acid at ambient temperature for 10 days, followed by chromatography. The sugar thus prepared was free from anhydride, did not crystallise, and consisted of a mixture of six tautomeric forms (see below).

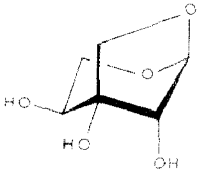
3-*C*-Hydroxymethyl-D-xylose, made by the method of Dahlman *et al.*[1], was a mixture of the sugar and the anhydride in nearly equal proportions, which were fractionated by chromatography. The anhydride **2** crystallised, and its ^{1}H- and ^{13}C-n.m.r. spectra were similar to those of the *gluco* derivative, the *J* values being almost identical.

The L-*lyxo* and D-*ribo* isomers have not been prepared, but Dr. Dahlman and Professor Garegg kindly provided the spectra of the crude products. In the ^{1}H-n.m.r. spectrum of 3-*C*-hydroxymethyl-L-lyxose, there was a pair of doublets at high field (3.4 p.p.m.) in the same position and with the same *J* values (9.3 and 10.7 Hz) as those of H-5*ax* in the spectrum of the *xylo* anhydride. Such *J* values cannot be given by the pyranose forms [which are in the $^4C_1$(L) conformation, see below] or the furanose forms and, therefore, this is a signal of the anhydride **3** which represents ~25% of the mixture. In the spectra of the *ribo* isomer, only the signal for H-1 of the anhydride **4** was detected; it represents ~5% of the mixture.

It was intended to determine the proportion of the anhydride in the equilibrium mixture by g.l.c. after borohydride reduction in methyl sulfoxide, followed by acetylation of the resulting alditol without removal of boric acid[6]. This method works well with unbranched sugars, but the hydroxymethyl sugars gave no compound detectable by g.l.c. Apparently, the hydroxymethyl group at the branch point of the alditol provides a good site for tridentate complexation with boric acid, which prevents acetylation. The proportions of the sugar and its anhydride were determined by ^{1}H-n.m.r. spectroscopy.



1 R = CH_2OH
2 R = H



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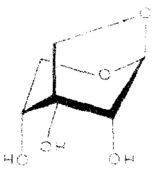

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The equilibria between aldoses and their 1,6-anhydrides have been studied[7]. Equilibration is rather slow: at 100° in 0.5M acid, it takes 1–2 days but some sugars react more rapidly, *e.g.*, idose and altrose reach equilibrium in ~6 h. It is apparent that the formation of the anhydride from 3-*C*-hydroxymethyl-D-glucose is faster. After only 15 min in 0.5M trifluoroacetic acid at 90°, 66% of the sugar was converted into the anhydride and 88% after 1 h. Signals of the sugar were barely detectable in the ^{1}H-n.m.r. spectrum of the 24-h reaction mixture. Starting with the crystalline anhydride, prolonged heating gave a mixture of 96% of the anhydride and 4% of the sugar. The hydroxymethylpentoses react at a lower rate and less of the anhydride is formed. The *xylo* isomer has 62% of the anhydride at equilibrium, the *lyxo* isomer 27%, and the *ribo* isomer ~8%. Equilibrium was not approached from the other side, but the reaction time appears sufficiently long to ensure that the mixture was close to equilibrium. The shorter times used by Dahlman *et al.*[3] for preparative purposes seem to have produced the same final composition.

The position of the equilibrium depends on the configuration and conformation of the sugar and the anhydride. The anhydride of 3-*C*-hydroxymethyl-D-glucose is similar to the 2,7-anhydride of *ido*-heptulose (which is formed[7] to the extent of 96%). It has the same substituents, albeit in different locations on the ring, and all are equatorial, which is the most favourable conformation. However, 3-*C*-hydroxymethyl-D-glucose is exceptional in having, in each pyranose form, an axial hydroxymethyl group that, moreover, is hindered (see below). Hence, the driving force to form the anhydride is great. Hydroxymethyl-xylose and -lyxose avoid the axial hydroxymethyl group by changing into the $^1C_4$ form. The *xylo* isomer then has two *syn*-axial hydroxyl groups, whereas the anhydride has none; hence, anhydride formation is favourable. On the other hand, the β-pyranose form of the *ribo* isomer has no serious interactions, but its anhydride has two *syn*-axial hydroxyl groups; hence, anhydride formation is limited. The *lyxo* isomer is intermediate between the *xylo* and the *lyxo* isomers. The results, therefore, are as expected.

*The composition of 3-*C*-hydroxymethylaldoses in solution.* — The n.m.r. spectra of the hydroxymethylaldoses in solution in D_2O are complex, and have not been analysed by Dahlman *et al.*[3]. Interpretation of the regions for H-1 and C-1 signals has now revealed the equilibrium compositions in D_2O.

The signals for H-1 of 3-*C*-hydroxymethyl-D-xylose (**2**) are shown in Fig. 1. Since the hydroxyl group of the side chain is γ to the aldehyde group, it can give rise to additional furanose forms. The classical example of a 3-*C*-hydroxymethylaldose is apiose, which has no pyranose but four furanose forms[8]. The sugars studied here are homomorphs of apiose, and the furanose H-1 signals can be assigned by comparison with those of apiose. The pyranose H-1 signals were assigned by comparison with those of an appropriate hexose. Thus, the chemical shifts (5.54, 5.33, 5.26, and 5.23 p.p.m.) of the four H-1 signals for the *xylo* isomer (Fig. 1) are close to those (5.56, 5.34, 5.28, and 5.26 p.p.m.) in the spectrum of apiose[8] and so are the J values (3.8, 4.6, 4.4, and 1.6 *versus* 3.8, 4.8, 4.2, and 1.2 Hz). The pyranoses are in the $^1C_4$ form and, therefore, comparison with xylose is inappropriate. Good correlation was found with the H-1 signals of the altropyranoses (δ 5.08, $J_{1,2}$ 0.9 Hz *versus* δ 5.09 and $J_{1,2}$ 1.3 Hz; δ 5.00, $J_{1,2}$ 4.2 *versus* δ 4.97 and $J_{1,2}$ 3.0 Hz). The spectrum in Fig. 1 also discloses the presence of a small proportion of the anhydride. A sample of this sugar completely free of the anhydride was not obtained.

A similar close analogy was found between the C-1 signals of the other branched-chain sugars and of apiose. In this way, all the C-1 signals were identified and the proportions of the various forms were determined (Table I). The furanose forms (**5**α, β-F for the *xylo* compound) that involve O-4 are described simply as "furanoses" and the additional forms that involve O-3^1 are denoted as 1,3^1-furanoses [**5**α,β(1,3^1)-F for the *xylo* compound]. The data obtained from the ^{13}C-n.m.r. spectra agree well with those from the ^{1}H-n.m.r. spectra (which confirms the correctness of our assignments).

In the ^{1}H-n.m.r. spectrum of 3-*C*-hydroxymethyl-D-glucose, the H-1 signals of the β-furanose and the α-pyranose overlap and their proportions were obtained from the ^{13}C-n.m.r. spectrum. The H-1 signals of the α- and the β-furanoses of the *lyxo* compound are very close to each other at δ 5.27 and their proportions were also obtained from the ^{13}C-n.m.r. spectrum. In the spectrum of D-lyxose, these signals occur at δ 5.24 and 5.26 and have similar J values (*cf.* 5.26 and 5.28 for dihydrostreptose[9]). Dihydrostreptose is the 5-deoxy derivative of 3-*C*-hydroxymethyl-L-lyxose and, since it cannot form pyranoses or an anhydride, only the furanose forms are found with an α:β ratio of 74:26 (the 1,3^1-furanoses were not detected in the spectrum[9,10]). The ratio obtained here from the ^{13}C-n.m.r. spectrum is similar.

Some aspects of the data in Table I deserve comment. Of the four forms of apiose, the more stable are those in which O-2,3 are *cis* (therefore, O-2 and the side chain are *trans*). The furanose forms (**5**F) of 3-*C*-hydroxymethyl-D-xylose, with O-2,3 *trans*, are more stable than the corresponding apioses because the furanose ring has closed through a secondary, rather than a primary, hydroxyl group[11]. Hence, their proportions in the branched-chain *xylo* sugar are considerably higher (26.5% each of the furanoses) than in apiose (14 and 16%). For the *gluco* isomer, the side chain in the 1,3^1-furanoses

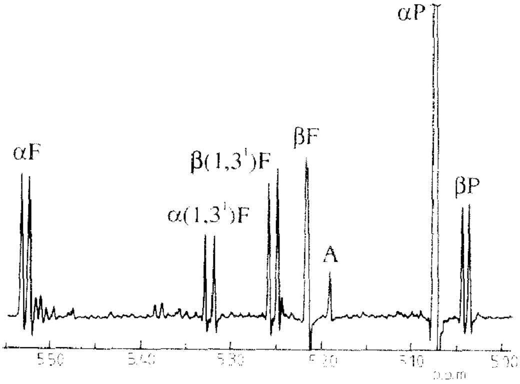
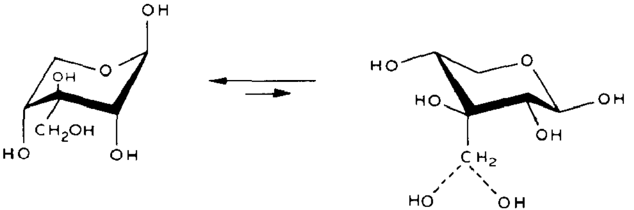
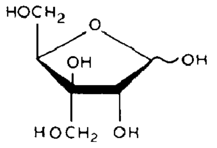


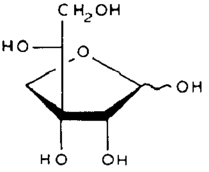
Fig. 1. The anomeric region of the ^{1}H-n.m.r. spectrum of 3-*C*-hydroxymethyl-D-xylose; A is the signal of the anhydride.



5β-P



5α,β-F



5α,β(1,3¹)-F

(comprising C-4,5,6) has an inevitable 1,3-parallel interaction; hence, the normal furanose forms preponderate. In the *lyxo* and *ribo* isomers, the furanose forms have O-2,3 *cis* and also benefit from ring closure through secondary hydroxyl groups; hence, the $1,3^1$-furanoses become very minor constituents of the equilibrium mixture.

It is clear from the $J_{1,2}$ value (4.2 Hz) that the β-pyranose form (**5**β-P) of the *xylo* isomer is in the $^1C_4$ conformation (the $^4C_1$ form would have $J_{1,2}$ ~8 Hz). There are two pairs of *syn*-axial hydroxyl groups in this conformation, and the presence of an axial hydroxymethyl group in the $^4C_1$ form does not appear to provide sufficient driving force for the ring inversion. However, O-3^1 will have a 1,3-parallel interaction with either O-2 or O-4 (both possibilities are shown in the formula), and this interaction further reduces the stability of the $^4C_1$ form. The α anomer ($J_{1,2}$ 0.9 Hz) will also be in the $^1C_4$ form, with one less, and the $^4C_1$ form, with one more, *syn*-axial interaction than the β anomer. The high proportion of the α-pyranose in the *gluco* isomer is surprising. With an O-1, C-3^1 interaction present, instability would be expected. It is possible that even this compound is partially in the $^1C_4$ conformation, which would increase its stability. The n.m.r. spectrum does not allow clear definition of the conformation and it could be partially in

TABLE I

The composition of 3-*C*-hydroxymethylaldoses in D_2O at 27°

3-C-Hydroxymethyl-	*α-P*	*β-P*	*α-F*	*β-F*	*α(1,3¹)-F*	*β(1,3¹)-F*
D-Glucose	19	32	17	21	3	8
D-Xylose	35.5	10.5	15	15	8.5	15.5
L-Lyxose	57	13	20	6	2.5	1.5
D-Ribose	18.5	70.5	3.5	4.5	1	1.5

a flexible form. The β-pyranose is in the $^4C_1$ form, since the other chair form would be most unfavourable.

The existence of the $1,3^1$-anhydrides could have been recognised some time ago. Rosenthal and Sprinzl[12] prepared the di-*O*-isopropylidene derivative of 3-deoxy-3-*C*-hydroxymethyl-D-allose and removed the protecting groups by heating with dilute acid. Chromatography then revealed three products, and the experiment was abandoned. It is likely that these products were the branched-chain sugar together with its 1,6- and $1,3^1$-anhydride. The three hydroxymethylpentoses prepared by Dahlman *et al.*[3] contained, before chromatography, abundant proportions of the $1,3^1$-anhydrides, as shown by the n.m.r. spectra. The authors commented that these anhydrides may be 1,5-anhydrofuranoses. 2,6-Dideoxy-4-*C*-(1-hydroxyethyl)-D-*erythro*-hexose, in which the side chain that contains the hydroxyl group is attached to C-4, readily forms the $1,4^1$-anhydride[13]. However, 4-*C*-hydroxymethyl-L-*threo*-pentose does not seem to yield a substantial proportion of the $1,4^1$-anhydride[14]. For this compound, the pyranose forms have no unfavourable interactions, and there is no inducement to form the anhydride.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler hot-stage microscope and are not corrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. Reactions were monitored and the purity of compounds checked by t.l.c. on silica gel (Uniplate HLF), using ethanol–ethyl acetate (4:1) and detection by charring with sulfuric acid. N.m.r. spectra were recorded with a Bruker AM-500 spectrometer at 27°.

1,3-Anhydro-3-C-hydroxymethyl-α-D-glucopyranose (**1**). — A solution of 3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[3] (150 mg) in 0.25M sulfuric acid was heated to 80° for 3 days, then neutralised ($BaCO_3$), filtered, and concentrated. Once seed crystals were available, the anhydride could be crystallised from ethanol–ethyl acetate. On the first occasion, a solution of the syrup in ethanol–ethyl acetate (1:3) was filtered and subjected to chromatography on Kieselgel 60H (Merck) with ethanol–ethyl acetate (1:6). The anhydride was eluted in the first fractions and crystallisation gave **1** (87 mg, 80%), m.p. 159°, $[\alpha]_D^{24}$ +13.2° (*c* 1.0, water). N.m.r. data (D_2O): ^{1}H, δ 5.23 (s, H-1), 4.12 (d, $J_{3^1endo,3^1exo}$ −8.2 Hz, H-3^1*endo*), 3.84 (dd, $J_{5,6'}$ 4.5 Hz, H-6′), 3.77 (dd, $J_{4,3^1exo}$ 1.75 Hz, H-3^1*exo*), 3.765 (dd, $J_{5,6}$ 2.4, $J_{6,6'}$ −12.4 Hz, H-6), 3.75 (dd, $J_{4,5}$ 9.1 Hz, H-4), 3.64 (s, H-2), 3.58 (ddd, H-5); ^{13}C, δ 105.1 (C-1), 81.1 (C-3), 74.67, 74.62 (C-4,5), 71.7 (C-2), 70.4 (C-3^1), and 63.15 (C-6).

Anal. Calc. for $C_7H_{12}O_6$: C, 43.75; H, 6.29. Found: C, 43.45, H, 6.42.

The tetra-acetate of **1**, prepared by acetylation with pyridine–acetic anhydride at ambient temperature for 4 days, had m.p. 122–123° (from ethanol), $[\alpha]_D^{22}$ +21° (*c* 1.4, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.50 (dd, $J_{4,5}$ 9.2, $J_{4,3^1exo}$ 1.75 Hz, H-4), 5.38, 5.33 (s, H-1,2), 4.44 (d, $J_{3^1endo,3^1exo}$ −8.5 Hz, H-3^1*endo*), 4.23 (dd, $J_{5,6}$ 2.6, $J_{6,6'}$ −12.3 Hz, H-6), 4.13 (dd, $J_{5,6'}$ 4.8 Hz, H-6′), 4.01 (dd, H-3^1*exo*), 3.89 (ddd, H-5), 2.10, 2.095, 2.09, 1.98 (H-Ac).

Anal. Calc. for $C_{15}H_{20}O_{10}$: C, 50.00; H, 5.59. Found: C, 49.65; H, 5.75.

*3-C-Hydroxymethyl-*D*-glucose.* — A solution of 3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[3] (150 mg) in 1,4-dioxane (2 mL), water (2 mL), and aq. 10% trifluoroacetic acid (1 mL) was stored for 10 days at ambient temperature, then concentrated. Column chromatography (ethanol–ethyl acetate, 1:6) of the residue gave, first, small amounts of the anhydride (R_F 0.43) and the mono-*O*-isopropylidene derivative (R_F 0.57), followed by the sugar, isolated as a syrup (80 mg, 73%), R_F 0.20–0.35), $[\alpha]_D^{24}$ +10.3° (*c* 2.8, water). N.m.r. data (D_2O): H-1 signals, δ 5.51 (d, $J_{1,2}$ 3.8 Hz, α-F), 5.315 [d, $J_{1,2}$ 5.1 Hz, α-(1,3^1)F], 5.24 [d, $J_{1,2}$ 4.2 Hz, β-(1,3^1)F], 5.20 (s and d, $J_{1,2}$ ~3 Hz, β-F and α-P), 4.965 (d, $J_{1,2}$ 8.3 Hz, β-P); H-2 signals, δ 4.14 [d, α-(1,3^1)F], 4.08 (s, β-F), 4.07 (d, α-F), 3.39 (d, β-P); numerous other signals at δ 4.2–3.5; C-1 signals, δ 104.95 (β-F), 104.1 [β-(1,3^1)F], 99.35 (α-F), 96.3 [α-(1,3^1)F], 97.0 (α-P), 94.65 (β-P); other β-P signals at 79.85, 77.65, 74.7, 64.2, and 62.9.

*1,3^1-Anhydro-3-*C*-hydroxymethyl-α-*D*-xylopyranose* (**2**). — Prepared according to Dahlman *et al.*[3], column chromatography (ethanol–ethyl acetate, 1:9) of the mixture of the sugar and anhydride gave **2**, m.p. 180–181°, $[\alpha]_D^{24}$ −40° (*c* 1.1, water). N.m.r. data (D_2O): ^{1}H, 5.20 (s, H-1), 4.13 (d, $J_{3^1exo,3^1endo}$ −8.2 Hz, H-3^1*endo*), 4.03 (dd, $J_{4,5eq}$ 6.8, $J_{5ax,5eq}$ −10.7 Hz, H-5*eq*), 4.01 (sept, $J_{4,5ax}$ 9.3, $J_{3^1exo,4}$ 1.7 Hz, H-4), 3.765 (dd, H-3^1*exo*), 3.65 (s, H-2), 3.40 (dd, H-5*ax*); ^{13}C, δ 105.02 (C-1), 81.36 (C-3), 77.67 (C-4), 71.30 (C-2), 70.23 (C-3^1), and 65.98 (C-5).

*N.m.r. spectra (D_2O) of the 3-*C*-hydroxymethylpentoses.* — (*a*) *3-*C*-Hydroxymethyl-*D*-xylose.* H-1 signals, δ 5.535 (d, $J_{1,2}$ 3.8 Hz, α-F), 5.33 [d, $J_{1,2}$ 4.6 Hz, α-(1,3^1)F], 5.26 [d, $J_{1,2}$ 4.4 Hz, [β-(1,3^1)F], 5.225 (d, $J_{1,2}$ 1.6 Hz, β-F), 5.08 (d, $J_{1,2}$ 0.9 Hz, α-P), and 5.04 (d, $J_{1,2}$ 4.2 Hz, β-P); C-1 signals, δ 104.85 (β-F), 104.65 [β-(1,3^1)F], 99.0 (α-F), 97.65 [α-(1,3^1)F], 96.65 (β-P), and 95.2 (α-P); other ^{13}C signals for α-P at δ 77.55, 73.2, 70.85, 69.35, and 66.0.

(*b*) *3-*C*-Hydroxymethyl-*L*-lyxose.* H-1 signals, δ 5.56 [d, $J_{1,2}$ 3.5 Hz, β-(1,3^1)F], 5.275 (d, $J_{1,2}$ 5.0 Hz, β-F), 5.27 (d, $J_{1,2}$ 4.6 Hz, α-F), 5.24 [s, α-(1,3^1)F], 5.01 (d, $J_{1,2}$ 3,8 Hz, β-P), 4.80 (d, $J_{1,2}$ 8.0 Hz, α-P); H-2 of α-P: δ 3.48 (d); anhydride: δ 5.03 (d, $J_{1,2}$ 3.4 Hz, H-1), 3.40 (dd, $J_{4,5ax}$ 9.3, $J_{5ax,5eq}$ −10.7 Hz, H-5*ax*); C-1 signals, δ 105.2 [α-(1,3^1)F], 102.4 (α-F), 97.0 (β-F), 96.0 (α-P), 94.4 (β-P); other ^{13}C signals for α-P at δ 71.9, 70.1, 67.8, 64.9; anhydride, δ 99.7 (C-1), 76.8, 75.0, 70.1 (C-3^1), and 66.5 (C-5).

(*c*) *3-*C*-Hydroxymethyl-*D*-ribose* (spectra from Dr. Dahlman). H-1 signals, δ 5.54 [d, $J_{1,2}$ 4.0 Hz, α-(1,3^1)F], 5.36 (d, $J_{1,2}$ 4.9 Hz, α-F), 5.25 (s, β-(1,3^1)F], 5.21 (d, $J_{1,2}$ 4.9 Hz, β-F), 5.08 (d, $J_{1,2}$ 3.7 Hz, α-P), 4.80 (d, $J_{1,2}$ 8.0 Hz, β-P); anhydride, δ 5.20 (d, $J_{1,2}$ 2.7 Hz, H-1); δ 3.38 (d, H-2 of β-P); C-1 signals, δ 102.8 (β-F), 97.2 (α-F), 96.0 (β-P), and 94.3 (α-P); the other furanose signals were not observed; other ^{13}C signals for β-P at δ 72.0, 67.0, 65.1, and 62.0; other ^{13}C signals for α-P at δ 76.4, 68.5, 60.1; C-1 of the anhydride at δ 100.8.

Determination of the equilibrium composition. — Samples (~7 mg, obtained from Dr. Dahlman) of 5-*O*-acetyl-3-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-xylofuranose, 3-*C*-acetoxymethyl-5-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-β-L-lyxofuranose, and 3-*C*-acetoxymethyl-5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-ribofuranose[3] were each heated in 0.5M trifluoroacetic acid to 90° for 40 h. Each hydrolysate was concentrated and the composition of each residue, evaluated by ^{1}H-n.m.r. spectra, revealed 63, 27, and ~8% of anhydride, respectively. 3-*C*-Hydroxymethyl-D-xylose (5 mg) was heated similarly for 24 h and the product contained 61% of anhydride. These spectra were also used to determine the composition of each aldose in solution. The long heating caused some decomposition: signals of impurities were seen in the spectra.

1,3^{1}-Anhydro-3-*C*-hydroxymethyl-D-glucose (14 mg) was heated with 0.5M trifluoroacetic acid (2 mL) at 90° for 60 h. The ^{1}H-n.m.r. spectrum, with a long iteration period and 256 sweeps, of the product revealed 4% of the free sugar.

ACKNOWLEDGMENTS

The authors thanks Dr. O. Dahlman and Professor P. J. Garegg for the gift of samples and for copies of their n.m.r. spectra.

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