CONFORMATION OF ACYCLIC DERIVATIVES OF SUGARS

PART VIII.* CONFORMATIONS OF THE 2,3,4,5-TETRA-*O*-ACETYLPENTOSE DIMETHYL ACETALS IN SOLUTION†

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ABSTRACT

The conformations of the peracetylated aldopentose dimethyl acetals having the D-*ribo* (**1**), L-*arabino* (**2**), D-*xylo* (**3**), and D-*lyxo* (**4**) configurations have been studied in chloroform-*d* solution by n.m.r. spectroscopy at 100 and 220 MHz. The *arabino* derivative **2** adopts a planar, zigzag conformation almost exclusively, whereas the other three examples adopt conformations in which parallel 1,3-interactions between substituents, that would be present in the extended forms, are relieved. In the *lyxo* derivative **4**, rotation about C-1–C-2 from the extended form is involved. The *ribo* derivative **1** tends to adopt a sickle conformation through rotation about C-2–C-3 to bring C-1 out of the approximate plane of the other atoms in the chain; the *xylo* derivative behaves similarly, but with rotation about C-3–C-4 to bring C-5 out of the plane. The derivatives **1**–**4** exhibit mass-spectral fragmentation pathways very similar to those of the peracetylated aldose diethyl dithioacetals.

INTRODUCTION

Studies on acyclic derivatives of sugars in solution by n.m.r. spectroscopy have shown that the sugar chain tends to adopt a favored conformation having the chain of carbon atoms in a planar, zigzag arrangement[2], unless such a conformation would generate a parallel 1,3-interaction between oxygen atoms, in which case the favored conformation is one in which this interaction is alleviated by rotation about one of the carbon–carbon bonds to bring the molecule into a bent or "sickle" conformation[1,3–5]. This concept has been found valid in several complete configurational series of derivatives, including the peracetylated aldopentose diethyl dithioacetals[5], the *aldehydo*-pentose tetraacetates[1], the acetylated methyl 5-hexulosonates[6], and the pentononitrile tetraacetates[7], and in several partial series, including acetylated

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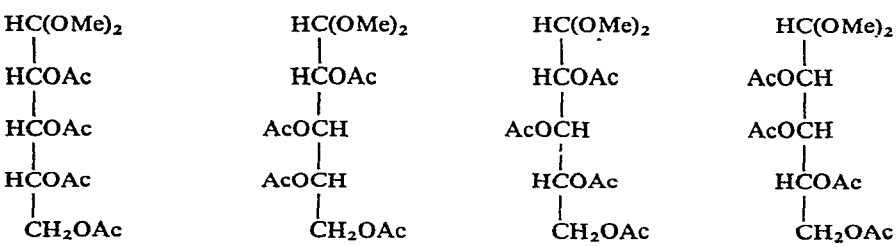
diphenyl dithioacetals[8], acetylated[9] and nonacetylated[3] glyculose arylosotriazoles, tetraacetoxy-*trans*-1-nitro-1-hexenes[10], aldose diethyl dithioacetals[11], acetylated alditols[12], acetylated (polyhydroxyalkyl)-thioamides and -thiazoles[13], and (polyhydroxyalkyl) quinoxaline derivatives[4]. Similar considerations apply in the crystalline state, as shown especially by the extensive studies by Jeffrey and associates on alditols[14] and other acyclic systems; details are given in a review article[15]. A correlation has been pointed out[16,17] between the relative propensities of acyclic sugar derivatives to undergo oxolane ring-forming reactions under conditions of kinetic control, and their tendencies to adopt either the extended or the sickle conformation; similar factors may possibly account for the observed[18] order of reactivities (ribose > xylose > lyxose > arabinose), whereby the aldopentoses are converted into 2-furaldehyde by the action of strong acid.

The present report describes a comparative conformational study, in solution, of the acetylated dimethyl acetals of the four aldopentose configurations. Observations in this series are shown to be in full accord with the principles earlier delineated, wherein the extended conformation is favored only when it does not lead to a 1,3-interaction between substituents.

DISCUSSION

Preparation of acetylated aldopentose dimethyl acetals. — The four tetra-*O*-acetylaldopentose dimethyl acetals, having the D-*ribo*[19] (**1**), L-*arabino* (**2**), D-*xylo*[19] (**3**), and D-*lyxo*[19] (**4**) configurations, were prepared from dithioacetal precursors by treatment in methanolic solution with mercuric chloride in the presence of cadmium carbonate. The starting dithioacetals were selected on the basis of their availability. The known tetra-*O*-acetyl-L-arabinose diethyl dithioacetal[20] and tetra-*O*-acetyl-D-xylose diethyl dithioacetal[21] were used for preparing compounds **2** and **3**, respectively. The general procedure[20] used for preparing tetra-*O*-acetyl-L-arabinose diethyl dithioacetal was used for converting D-ribose di-isobutyl dithioacetal[22] and the D-lyxose analog[23] into their syrupy tetraacetates, which were then converted into the dimethyl acetals **1** and **4**, respectively by the technique[24] described for the corresponding D-glucose derivative. Use of the literature procedure[19] actually described for the peracetylated aldopentose dimethyl acetals in the D-ribose, L-arabinose, and D-xylose series led to complex mixtures from which the desired acetals could not be



1 **2** **3** **4**

separated pure. In contrast, the method[24] used here led to simpler mixtures in which the required acetals greatly preponderated over side products. The acetals could be separated readily, either by crystallization or by column chromatography. The D-ribose derivative **1** was obtained analytically pure for the first time, as a distilled oil. The L-arabinose derivative **2** was obtained crystalline, and had physical constants in accord with those recorded[19] for the D enantiomorph. The pure D-xylose derivative (**3**), obtained as a distilled oil, had a specific rotation (+3.9° in chloroform) substantially different from that recorded[19] (+30.6° in chloroform). The D-lyxose analog (**4**) was obtained as a distilled oil having a specific rotation in accord with the literature value.

The mass spectra of compounds **1–4** are all very similar, and parallels can be drawn between the fragmentations observed and those recorded[25] for the acetylated aldose dithioacetals. Thus, there is observed a weak, molecular-ion peak (*m/e* 364), and a peak at *m/e* 333 corresponding to $M^+ \cdot - \cdot OCH_3$. A series of peaks observed at *m/e* 217, 145, and 73 can be assigned to fragmentations from the molecular ion by cleavage at C-2–C-3, C-3–C-4, and C-4–C-5, respectively. Other significant ions are observed at *m/e* 43 (CH_3CO^+), 75 (MeOCH=$\overset{+}{O}$Me), and 305 ($M^+ \cdot - \cdot OAc$), together with an ion, *m/e* 259, that can be assigned to a 3,4-diacetoxy-2-(acetoxymethyl)tetrahydrofurylium fragment. These fragmentation modes are summarized in Chart I.

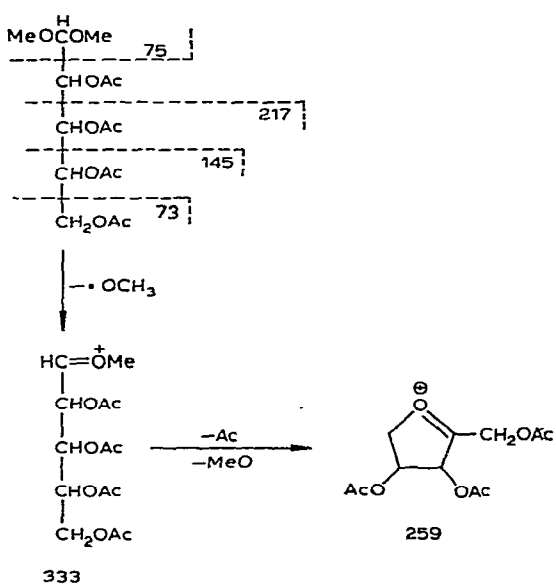


Chart I. Mass-spectral fragmentation modes for acetylated aldopentose dimethyl acetals.

N.m.r. spectra. — The spectra of the acetals **1–4**, measured in chloroform-*d* at ~30°, confirmed that the compounds were pure and contained no side-products giving rise to detectable peaks. Each compound showed a high-field group of closely

spaced singlets near τ 8.0 for the 12 protons of the acetyl groups, and a pair of non-equivalent, 3-proton singlets near τ 6.7 for the two methoxyl groups. At lower field, there was observed a 3-proton multiplet near τ 5.8 and a second 3-proton multiplet between τ 4.5 and 5.0. The former multiplet was assigned to H-1 and the C-5 methylene group, and the latter to H-2, 3, and 4. At 100 MHz, the spectra of the L-*arabino* (**2**), D-*lyxo* (**4**), and D-*xylo* (**3**) derivatives could be analyzed readily on a first-order basis, but it was necessary to obtain a spectrum at 220 MHz to permit first-order analysis for the D-*ribo* derivative (**1**). In each example, the H-1 signal was observed as a doublet in the same spectral region as that of the C-5 proton signals, so that the H-1 signal sometimes overlapped the eight-line pattern (the AB portion of an ABX system) near τ 5.8 caused by H-5 and H-5'. In the multiplet at low field (H-2, 3, and 4), the lowest-field signal in each example was a quartet assigned to H-3; the quartet assigned to H-2 was at highest field in this group, except for the D-arabinose derivative **2**, for which the H-2 quartet was immediately upfield of the H-3 signal. The H-4 signal showed, in each case, the expected multiplicity for the X-proton of an ABX system coupled also to H-3. The spectral regions for the six protons on the chain is illustrated in Fig. 1 for the L-*arabino* derivative **2**, and in Fig. 2 for the D-*ribo* derivative **1**. The first-order coupling constants determined from these spectra are recorded in Table I, and Table II gives the chemical shifts determined from the spectra.

TABLE I

CHEMICAL-SHIFT DATA[a] FOR COMPOUNDS **1**, **2**, **3**, AND **4** IN CHLOROFORM-*d*

Compound	*Configuration*	*Chemical shifts* (τ) *in chloroform-d*							
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*OMe*	*OAc*
1	*ribo*	5.51[b]	4.76[b]	4.58[b]	4.64[b]	5.58[b]	5.87[b]	6.66, 6.73	7.96, 7.99 (2), 8.01
2	*arabino*	5.75	4.80	4.55	4.94	5.79	5.99	6.70, 6.74	7.94, 7.96, 8.00 (2)
3	*xylo*	5.72	4.88	4.55	4.82	5.71	6.04	6.68, 6.72	7.95, 7.97, 8.00, 8.01
4	*lyxo*	5.64	4.88	4.59	4.66	5.78	6.01	6.64, 6.71	7.94, 7.98 (2), 7.99

[a]First-order values from 100-MHz spectra at ambient temperature, unless otherwise stated. [b]From 220-MHz spectrum at ambient temperature.

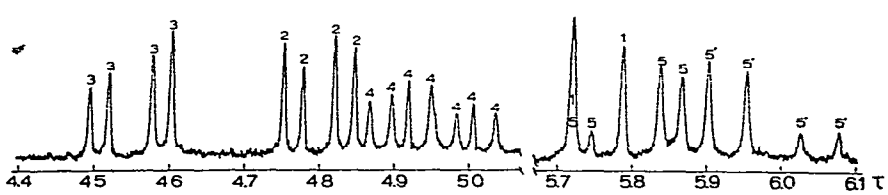


Fig. 1. The low-field portion of the 100-MHz n.m.r. spectrum of tetra-*O*-acetyl-L-arabinose dimethyl acetal (**2**) in chloroform-*d* at ~30°.

TABLE II

FIRST-ORDER COUPLING-CONSTANTS[a] FOR COMPOUNDS 1, 2, 3, AND 4 MEASURED IN CHLOROFORM-*d*

Compound	*Configuration*	*Coupling constants, Hz*					
		$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
1	*ribo*[b]	6.5	3.9	5.5	2.5	6.3	12.2
2	*arabino*	6.7	2.6	8.3	2.9	5.1	12.3
3	*xylo*	5.5	4.7	5.4	4.3	5.9	12.0
4	*lyxo*	5.6	6.5	3.3	4.4	6.3	11.6

[a]From 100-MHz spectra at ambient temperature, unless otherwise stated. [b]From 220-MHz spectrum at ambient temperature.

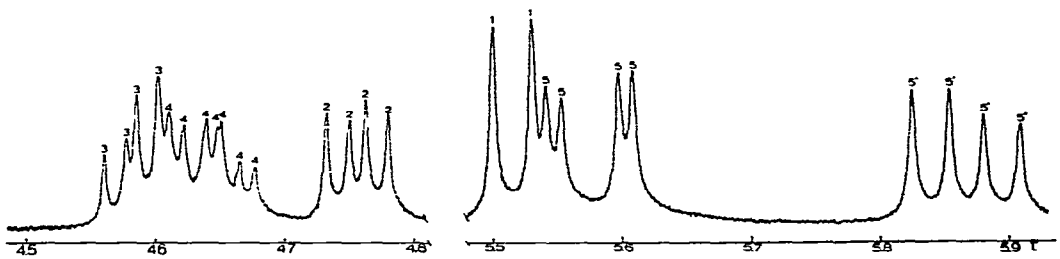
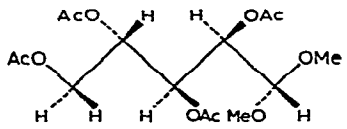


Fig. 2. The low-field portion of the 220-MHz n.m.r. spectrum of tetra-*O*-acetyl-D-ribose dimethyl acetal (**1**) in chloroform-*d* at ~30°.

Conformational significance of the n.m.r.-spectral data. — Following the rationale of earlier arguments[1,5], that is, by assuming that (*a*) rapid equilibrium between rotameric conformations exists in the derivatives **1–4**, (*b*) antiparallel protons exhibit spin–spin couplings of 8–9 Hz, and (*c*) gauche-disposed protons are coupled to the extent of 2–3 Hz, the following interpretations were made.

Arabinose derivative **2**. The key spin-couplings that define the shape of the backbone chain, namely, $J_{2,3}$ and $J_{3,4}$, are 2.6 and 8.3 Hz, respectively, indicating that H-2 and H-3 are exclusively gauche and that H-3 and H-4 are exclusively antiparallel. The contribution of the gauche arrangement of H-3 and H-4 is negligible, as is the contribution of the antiparallel arrangement of H-2 and H-3, because the couplings observed are extreme values. The $J_{1,2}$ coupling (6.7 Hz) indicates that the antiparallel disposition of H-1 and H-2 is preponderant if not exclusive; the fact that it does not reach the magnitude of $J_{3,4}$ can be interpreted as suggesting that (*a*) about 70% of the antiparallel form exists in equilibrium with one or both gauche rotamers, (*b*) electronegativity factors[26] decrease the value of $J_{1,2anti}$, or (*c*) there is some torsional distortion, along C-1–C-2, away from the fully staggered arrangement. Detailed quantitative interpretations based solely on the concept of rotameric equilibria, such as have been advanced[13] in similar situations, scarcely appear justified, unless adequate consideration is accorded the other two possible factors just mentioned. The

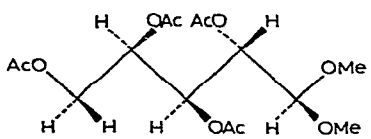


2a

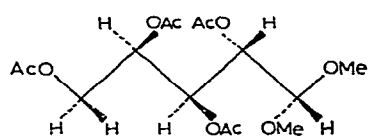
values of $J_{4,5}$ and $J_{4,5'}$ (2.9 and 5.1 Hz, respectively) indicate that one proton at C-5 is gauche to H-4 and that the other one, although not exclusively antiparallel to H-4, is preponderantly so.

The spin-coupling data for compound **2** thus accord with a favored conformation in which the chain is fully extended, as shown in **2a**. This arrangement has no parallel 1,3-interactions of substituents. The rotameric states shown along C-2–C-3, and along C-3–C-4 appear to be populated almost exlusively, but some distortion or freedom to occupy other states appears possible along C-1–C-2 and along C-4–C-5. Accepting the probability of a rotameric equilibrium, it may be speculated that the form having one C-5 proton antiparallel to H-4 exists in about equal proportion with that form having O-5 antiparallel to H-4 (the other possible rotamer would experience an unfavorable 1,3-interaction between O-5 and O-3). Undoubtedly, there are minor distortions from the ideal planar, extended form, but the n.m.r.-spectral technique is a tool insufficiently sensitive to detect such distortions.

Lyxose derivative **4**. The $J_{2,3}$ and $J_{3,4}$ spin-couplings (6.5 and 3.3 Hz, respectively) indicate that H-2 and H-3 are preponderantly antiparallel (although a contribution of about 30% of a form having H-2 and H-3 gauche-disposed appears probable) and that H-3 and H-4 are almost exclusively gauche. Taking into consideration the remaining couplings, the planar, extended conformation **4a** can be regarded as a major contributing conformation, but the low value (5.6 Hz) of $J_{1,2}$ indicates that there is a substantial population (possibly up to 50%) of rotameric states wherein H-1 and H-2 are not antiparallel. This behavior can be attributed to the fact that, in the conformation **4a**, a parallel 1,3-interaction exists between O-3 and one of the methoxyl groups at C-1; this destabilization can be relieved by rotation about C-1–C-2 to afford the conformation **4b**. The somewhat low value for $J_{2,3}$ indicates, furthermore, that an alternative, if quantitatively less significant, route for relief of this interaction is by rotation about C-2–C-3. The values observed for $J_{4,5}$ and $J_{4,5'}$ indicate that the conformer having H-4 antiparallel to one proton at C-5 is preponderant, but that another rotameric state (presumably also having O-5 gauche to H-4) makes a substantial contribution to the conformational population.

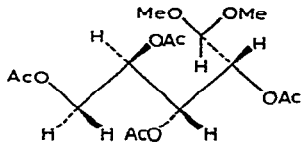


4a



4b

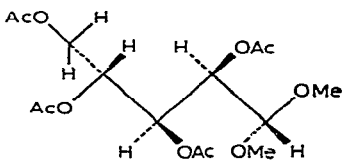
Ribose derivative **1**. The spin couplings observed are in no way consistent with an extended conformation, because this would place H-2 and H-3 antiparallel, and the observed value of $J_{2,3}$ is only 3.9 Hz. Such a conformation would have a parallel 1,3-interaction between O-2 and O-4. The couplings observed accord best with a



1a

favored conformation consisting of the sickle arrangement (**1a**) derived from the planar form by rotation about C-2–C-3 to bring H-2 and H-3 into a gauche disposition without generation of a 1,3-interaction between C-1 and O-4. In addition, other, nonextended conformers evidently contribute appreciably, as the $J_{3,4}$ value (5.5 Hz) is consistent with significant population of a rotameric state in which the O-2–O-4 interaction is relieved by having H-3 and H-4 gauche; furthermore, there is probably some contribution from forms not having H-1 and H-2 antiparallel.

Xylose derivative **3**. As with the ribose derivative **1**, the spin couplings observed for **3** exclude the possibility of an extended conformation; such an arrangement would require H-3 and H-4 to be gauche, whereas the observed $J_{3,4}$ value is 5.4 Hz. The extended conformation would give rise to a parallel 1,3-interaction between O-2 and O-4. The derivative **3** evidently favors sickle conformation **3a**, derived from the



3a

extended form by rotation about C-3–C-4 to alleviate the O-2–O-4 interaction without creation of a new interaction between O-2 and C-5. Again, in resemblance to the ribose derivative, contributions of other nonextended forms are evidently involved in the total conformational population of compound **3**; thus, the $J_{2,3}$ value (4.7 Hz) indicates some extent of population of a conformer having H-2 and H-3 antiparallel, and the $J_{1,2}$ value (5.5 Hz) shows that H-1 and H-2 are not exclusively antiparallel. It can be expected that a dynamic equilibrium exists in which conformation **3a** is populated extensively, but not exclusively, and that other participating conformational states are populated to the extent that 1,3-interactions and, to a lesser extent, gauche interactions between substituents are minimized.

General correlations. — The foregoing data are entirely concordant with those established for the corresponding dithioacetal analogs[5]. They show that the extended conformation is strongly favored in the *arabino* series, whereas, in the *lyxo* series, this conformation experiences destabilization through a parallel 1,3-interaction,

involving the end of the chain, that causes some predisposition toward a nonextended conformation. This effect becomes still more severe in the *ribo* and *xylo* series, where the extended form is strongly disfavored; sickle forms having C-1 and C-5, respectively, out of the plane of the other carbon atoms of the chain become the major species in conformational populations wherein avoidance of parallel 1,3-interactions appears to be the major influential factor. These data further support rationalizations, extended to considerations of transition-state energies, that correlate the ease with which acyclic sugar derivatives adopt nonextended conformations (thus orienting the groups more favorably for ring-forming reactions) with their relative tendencies to undergo irreversible cyclization to form the oxolane ring[27]. On treatment of pentose dialkyl dithioacetals with *p*-toluenesulfonyl chloride in pyridine, only the *arabino* derivative does not give a 2,5-anhydride[16]. Similarly, in the acid-catalyzed methanolysis of 1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonylaldopentoses to give 2,5-anhydroaldopentose dimethyl acetals, it is again the *arabino* derivative that exhibits the greatest reluctance to form the 2,5-anhydro ring[17]. It is tempting to speculate that, in the acid-catalyzed dehydration of aldopentoses to 2-furaldehyde, an acyclic, protonated *aldehydo*-aldopentose is the immediate precursor in the ring-closing step between O-2 and C-5, and that the observed[18] order of reactivity (*ribo* > *xylo* > *lyxo* > > *arabino*) reflects the relative ease with which these intermediates can reach the necessary transition-state geometry.

EXPERIMENTAL

General methods. — Solutions were concentrated by means of a rotary evaporator at temperatures not exceeding 40°. The progress of reactions was monitored by t.l.c. with silica gel Merck F_{254} and 3:1 dichloromethane–ether as eluant, and the homogeneity of all products was verified by use of the same system. Non-crystalline products were purified on columns of silica gel Merck (Type 7734, 50–200 μm) with the same eluant. Melting points were measured with a Leitz hot-plate microscope, and are corrected. Optical rotations were measured by use of a "Quick-Polarimètre" (Roussel et Jouan). N.m.r. spectra were recorded at 100 MHz by MM. Bouhet or Nardin at the Centre d'Études Nucléaires de Grenoble (Service de Chimie Organique Physique) and at 220 MHz by The Canadian 220 MHz NMR Centre, Ontario Research Foundation, Sheridan Park, Canada. Mass spectra were determined by M. Gueraud at the Centre d'Études Nucléaires de Grenoble, under the direction of M. Ulrich.

Tetra-O-*acetyl*-D-*ribose di-isobutyl dithioacetal.* — Prepared from the non-acetylated precursor[22] by the procedure described[20], and purified by column chromatography, this product was obtained, in almost quantitative yield, as an oil, $[\alpha]_D^{24}$ +21.5° (*c* 1, chloroform).

Anal. Calc. for $C_{21}H_{36}O_8S_2$: C, 52.47; H, 7.54; S, 13.34. Found: C, 52.29; H, 7.40; S, 13.45.

Tetra-O-*acetyl*-D-*lyxose di-isobutyl dithioacetal.* — This product, prepared[20]

from the non-acetylated precursor[23] as in the preceding experiment, was obtained, in almost quantitative yield, as an oil, $[\alpha]_D^{24}$ +35.5° (*c* 1, chloroform).

Anal. Calc. for $C_{21}H_{36}O_8S_2$: C, 52.47; H, 7.54; S, 13.34. Found: C, 52.63; H, 7.53; S, 13.52.

Tetra-O-acetylaldopentose dimethyl acetals. — General procedure. The tetra-*O*-acetylaldopentose dialkyl dithioacetal (10 mmoles) was dissolved in abs. methanol (45 ml), cadmium carbonate (35 mmoles) was added, and a solution of mercuric chloride (60 mmoles) in abs. methanol (35 ml) was slowly added, with stirring, at room temperature. After completion of the addition, the mixture was maintained with stirring at reflux temperature, and the progress of the reaction was monitored by t.l.c.

The optimal time of reaction was judged to be 3 h for the *arabino*, *lyxo*, and *ribo* derivatives, and 24 h for the *xylo* derivative. At the appropriate time for each reaction, the mixture was cooled and filtered, and the filtrate was evaporated in the presence of cadmium carbonate. The resultant paste was leached with chloroform, the solids were filtered off, and the filtrate was successively washed with 10% aqueous potassium iodide and water, dried (sodium sulfate), and evaporated to a product that showed, by t.l.c., the anticipated acetal, together with at least two side-products. Purification was effected by column chromatography, to furnish the desired, pure acetal.

Tetra-O-acetyl-D-ribose dimethyl acetal (**1**). From 4.0 g of tetra-*O*-acetyl-D-ribose di-isobutyl dithioacetal was obtained 2.35 g of an oil showing, by t.l.c., three components, having R_F 0.60, 0.44, and 0.35. Resolution on a column containing 60 g of silica gel gave, after passage of 120 ml of the eluant, the pure acetal **1**; yield 1.36 g (45%), $b_{0.05}$ 120–130°, $[\alpha]_D^{24}$ +20.4° (*c* 1.3, chloroform), R_F 0.60, n_D^{23} 1.4370 [lit.[19] $[\alpha]_D^{20}$ +18.0° (in chloroform)].

Anal. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.63. Found: C, 49.72; H, 6.46.

A mixture (627 mg) of the two slower-migrating components was eluted by passage of further eluant to a total of 200 ml.

Tetra-O-acetyl-L-arabinose dimethyl acetal (**2**). From the diethyl dithioacetal precursor[20] (3.22 g) was obtained 2.58 g of an oil that, by t.l.c., showed 3 components (R_F 0.48, 0.30, and 0.17). Crystallization from ether–petroleum ether gave the acetal **2**; yield 1.84 g (76%), m.p. 81–82°, $[\alpha]_D^{28}$ −22.5° (*c* 1.2, chloroform); R_F 0.48 (lit.[19] for the D enantiomorph, m.p. 77°, $[\alpha]_D^{22}$ +23° in chloroform).

Anal. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.63. Found: C, 49.46; H, 6.66.

Tetra-O-acetyl-D-xylose dimethyl acetal (**3**). From 3.46 g of the diethyl dithioacetal precursor[21] was obtained an oil (2.74 g) showing at least 5 components (R_F 0.79, 0.70, 0.59, 0.32 and 0.27). Column chromatography of this mixture on 60 g of silica gel gave, after passage of 90 ml of eluant, the unchanged starting-material (R_F 0.79, 301 mg). Passage of 105 ml of solvent eluted a mixture (736 mg) of the components having R_F 0.79 and 0.70. The pure acetal **3**, R_F 0.59, was obtained after passage of 130 ml of eluant; yield 869 mg (29%), $b_{0.05}$ 120–130°, $[\alpha]_D^{22}$ +3.9° (*c* 1.5, chloroform); n_D^{26} 1.4410 (lit.[19] $[\alpha]_D$ +30.6° in chloroform).

Anal. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.63. Found: C, 49.36; H, 6.65.

The components having R_F 0.27 and 0.32 were eluted as a mixture (520 mg) after further elution to a volume of 175 ml.

Tetra-O-acetyl-D-lyxose dimethyl acetal (4). From 3.54 g of the di-isobutyl dithioacetal precursor was obtained 1.87 g of an oil that contained 3 components (R_F 0.52, 0.26, and 0.23). The desired product (4) was obtained by elution from a column of silica gel (40 g) after passage of 85 ml of eluant; yield 1.23 g (46%), $b_{0.04}$ 120–130°, $[\alpha]_D^{23}$ +21.8° (*c* 1.1, chloroform); R_F 0.52; n_D^{24} 1.4403 (lit.[19] $[\alpha]_D^{20}$ +21.6° in chloroform).

Anal. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.63. Found: C, 49.38; H, 6.80.

The other two components (469 mg) were eluted in admixture by passage of solvent up to 125 ml.

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