CONFORMATIONAL STUDIES ON PYRANOID SUGAR DERIVATIVES BY N.M.R. SPECTROSCOPY. THE CONFORMATIONAL EQUILIBRIA OF THE 1,2-*trans* PERACETYLATED ALDOPENTOPYRANOSYL BENZOATES AND PERBENZOYLATED ALDOPENTOPYRANOSYL ACETATES IN SOLUTION*†

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(Received January 7th, 1971)

ABSTRACT

2,3,4-Tri-*O*-acetyl-D-aldopentopyranosyl benzoates having the *β-ribo* (**1**), *α-arabino* (**2**), *β-xylo* (**3**), and *α-lyxo* (**4**) configurations, and 2,3,4-tri-*O*-benzoyl-D-aldopentopyranosyl acetates having the *β-ribo* (**5**), *α-arabino* (**6**), *β-xylo* (**7**), and *α-lyxo* (**8**) configurations have been prepared, and their conformations studied in acetone-d_6 or chloroform-*d* by n.m.r. spectroscopy at room temperature. Comparison of the results with similar data for the eight D-aldopentopyranose tetraacetates and tetrabenzoates indicates that the axial-directing effects of the OAc and OBz groups at C-1 are not independent of the total stereochemistry, nor are they independent of the nature of the acyloxy groups at C-2, 3, and 4. A concept of attractive interactions between *syn*-diaxial benzoyloxy groups provides a rationalization of the quantitative trends observed. The signal field-position of an acetyl group at O-1 is not subject to a strong upfield shift by the presence of benzoyloxy groups at C-2, 3, and 4, nor does a 1-*O*-benzoyl group cause specific shielding of acetoxy groups at C-2, 3, and 4.

INTRODUCTION

As part of a study of the conformations of pyranoid sugar derivatives, we reported[2] the measurement, by high-resolution n.m.r. spectroscopy, of the chair–chair conformational equilibria for the eight D-aldopentopyranose tetraacetates and the eight corresponding tetrabenzoates in acetone-d_6 solution. The results obtained for the two complete configurational series of sugar derivatives were discussed in terms of the steric and electronic effects of multiple acyloxy substituents on the conformational and configurational stability of tetrahydropyran ring-systems. A significant observation was that, for the tetrabenzoates relative to the tetraacetates, there was

*Supported, in part, by Grant No. GP-9646 from the National Science Foundation.
†For previous papers in this series, see Refs. 1–3 and references cited therein. For a preliminary report, see Ref. 4.
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usually a shift in the equilibrium position in the direction of that conformer having the bond to the C-1 substituent axial. The difference in the conformational population between an aldopentopyranose tetraacetate and the analogous tetrabenzoate was found to depend on the total stereochemistry. The only exception to the observed trend occurred with the α-D-*ribo* configuration, where the proportion of the conformer having the bond to the C-1 substituent equatorial was somewhat larger for the tetrabenzoate. An attractive interaction between the *syn*-diaxial benzoyloxy groups at C-2 and C-4 in the *1C*(D) conformer of α-D-ribopyranose tetrabenzoate was suggested as a factor controlling this reversal of the general trend.

The shifts in the conformational equilibria were interpreted in terms of differences in electronic and steric interactions in the tetraacetates and tetrabenzoates. As the conformational free-energies of the acetoxy and benzoyloxy groups at room temperature are, within experimental error, equal[5], the non-bonded gauche and *syn*-diaxial interactions present in the tetraacetates should not differ significantly from those in the tetrabenzoates. Steric interactions involving benzoyloxy groups might be very slightly smaller than for acetoxy groups, because of the greater electron-withdrawing ability of the benzoyl group, but the main factors responsible for differences in relative conformational populations in the two configurational series appeared to be electronic.

Among the electronic interactions considered was the dipolar effect that favors the axial disposition of an electronegative C-1 substituent (anomeric effect[6]). The shift in the conformational equilibria for the tetrabenzoates toward the conformer having the anomeric substituent axial could be explained qualitatively on the basis of a larger axial-directing influence of a C-1 benzoyloxy group, but this simple argument does not explain the quantitative differences observed between the different examples. As predicted from Lemieux's interpretation of the anomeric effect[6,7], changing the 2,3,4-substituents from acetates to the more electronegative benzoates should enhance the axial-directing influence of the C-1 benzoyloxy group. To explain the quantitative variations, polar contributions from other than the anomeric center, and attractive interactions between *syn*-diaxial groups, were suggested as possible factors. The relative contributions of the various electronic factors involved could not, however, be evaluated without additional data on related systems.

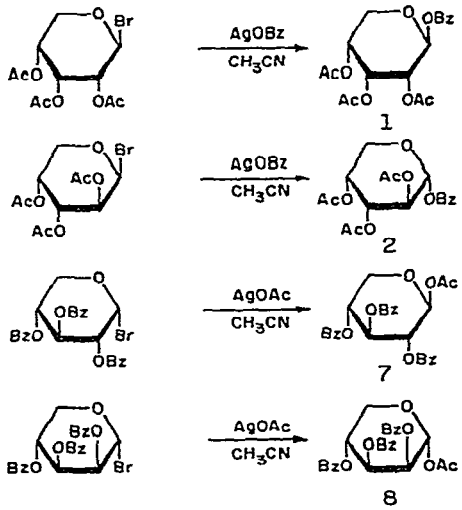
To shed further light on the role of competition between the anomeric and other polar effects in determining the conformational populations for the peracylated D-aldopentopyranoses, the conformational equilibria in acetone or chloroform solution have now been measured for the eight 1,2-*trans* D-aldopentopyranose mixed esters, four having at C-1 the group OAc and at C-2, C-3, and C-4 the OBz group, and four having at C-1 the group OBz and at C-2, C-3, and C-4 the OAc group.

MATERIALS AND METHODS

The 2,3,4-tri-*O*-acetyl-D-aldopentopyranosyl benzoates having the β-D-*ribo* (**1**), α-D-*arabino* (**2**), β-D-*xylo* (**3**), and α-D-*lyxo* (**4**) configurations were prepared by

treating a solution of the appropriate, thermodynamically "stable" tri-*O*-acetyl-D-aldopentopyranosyl bromide in acetonitrile with an equimolar amount of silver benzoate. The four mixed esters were obtained crystalline, and the *β-ribo* (**1**), *α-arabino* (**2**), and *α-lyxo* (**4**) derivatives are reported for the first time. The 2,3,4-tri-*O*-benzoyl-D-aldopentopyranosyl acetates, having the *β*-D-*ribo* (**5**), *α*-D-*arabino* (**6**), *β*-D-*xylo* (**7**), and *α*-D-*lyxo* (**8**) configurations, were similarly prepared by treating a solution of the appropriate, thermodynamically "stable" tri-*O*-benzoyl-D-aldopentopyranosyl bromide in benzene or acetonitrile with silver acetate. These four mixed esters are reported for the first time. The *α-arabino* (**6**) and *β-xylo* (**7**) derivatives were obtained crystalline, and the *β-ribo* (**5**) and *α-lyxo* (**8**) compounds, as amorphous glasses.

The eight mixed esters prepared under these conditions are the kinetic products resulting from neighboring-group participation[8,9] of the 2-acyloxy substituent (see Scheme I).



Scheme 1

The n.m.r. spectra were measured at 100 MHz on 20% (w/v) solutions of the freshly prepared compounds in acetone-d_6 or chloroform-*d* containing 5% of tetramethylsilane. The chemical shifts, given on the τ scale, were obtained by analysis of the spectra on a first-order basis, and are considered accurate to within ± 0.005 p.p.m. The time-averaged, $J_{4,5}$ and $J_{4,5'}$ spin-couplings employed in the calculation of conformational populations were obtained by ABX analysis[10] of spectra measured at 100-Hz sweep-width. The values reported are considered accurate to within ± 0.1 Hz. All other coupling-constants recorded were obtained on a first-order basis as direct peak-spacings from spectra measured at a sweep-width of 100 Hz, and are considered precise to within ± 0.1 Hz. Spectral data for the eight compounds are tabulated in Tables I and II. Partial n.m.r. spectra for compounds **2**, **4**, **5**, and **6** are given in Figs. 1–4, respectively.

TABLE I

FIRST-ORDER CHEMICAL SHIFTS[a] OF 1,2-*trans* PERACETYLATED ALDOPENTOPYRANOSYL BENZOATES AND PERBENZOYLATED ALDOPENTOPYRANOSYL ACETATES IN ACETONE-d_6 AT 31°

Compound	*Chemical shifts*[b] (τ)							
	H-1	*H-2*	*H-3*	*H-4*	[e]*H-5*	[e]*H-5'*	*Acetyl methyl*	*Benzoyl*
Tri-*O*-acetyl-β-D-ribopyranosyl benzoate (**1**)	3.75d	4.77m	4.37t	4.79m	5.81q	6.08q	7.96, 7.97[d]	1.90–2.62
Tri-*O*-acetyl-α-D-arabinopyranosyl benzoate (**2**)[e]	4.06d	4.55q	4.75q	4.63sx	5.89q	6.15q	7.86, 7.92, 7.97	1.90–2.71
Tri-*O*-acetyl-β-D-xylopyranosyl benzoate (**3**)	3.93d	4.85q	4.65t	5.01sx	5.79q	6.27q	7.95, 7.97, 8.00	1.93–2.58
Tri-*O*-acetyl-α-D-lyxopyranosyl benzoate (**4**)	3.74d	4.58t	4.50q	4.78sx	5.93q	6.16q	7.87, 7.95 7.96	1.87–2.54
Tri-*O*-benzoyl-β-D-ribopyranosyl acetate (**5**)	3.60d	4.42qn	4.02t	4.29m	5.51q	5.78q	7.83	1.99–2.76
Tri-*O*-benzoyl-α-D-arabinopyranosyl acetate (**6**)[e]	3.93d	——4.10—4.37m——			5.65q	5.96q	7.93	1.94–2.77
Tri-*O*-benzoyl-β-D-xylopyranosyl acetate (**7**)	3.76d	4.50q	4.07t	4.56sx	5.48q	5.99q	7.94	1.97–2.72
Tri-*O*-benzoyl-α-D-lyxopyranosyl acetate (**8**)	3.67d	4.24t	4.02q	4.22sx	5.67q	5.89q	7.80	1.90–2.77

[a]Data taken from spectra measured at 100 MHz. [b]Observed multiplicities: d, doublet; m, complex multiplet; q, quartet; qn, quintet; sx, sextet; t, triplet. [c]The proton on C-5 giving the higher field signal is designated H-5'. [d]6-Proton singlet. [e]In chloroform-*d*.

TABLE II

COUPLING CONSTANTS OF METHINE AND METHYLENE PROTONS FOR 1,2-*trans* PERACETYLATED ALDOPENTOPYRANOSYL BENZOATES AND PERBENZOYLATED ALDOPENTOPYRANOSYL ACETATES IN ACETONE-d_6 AT 31°

Compound	*Coupling constants*[a] (*Hz*)					
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	[b,c]$J_{4,5}$	[b,c]$J_{4,5'}$	$J_{5,5'}$
Tri-*O*-acetyl-β-D-ribopyranosyl benzoate (**1**)	4.9	3.5	3.4	3.3	5.9	−12.2
Tri-*O*-acetyl-α-D-arabinopyranosyl benzoate (**2**)[d]	6.0	8.4	3.2	4.2	2.2	−12.8
Tri-*O*-acetyl-β-D-xylopyranosyl benzoate (**3**)	5.9	7.6	7.5	4.5	7.7	−12.0
Tri-*O*-acetyl-α-D-lyxopyranosyl benzoate (**4**)	2.9	3.4	8.4	4.6	8.8	−11.7
Tri-*O*-benzoyl-β-D-ribopyranosyl acetate (**5**)[e]	3.3	3.8	3.6	2.4	3.8	−13.0
Tri-*O*-benzoyl-α-D-arabinopyranosyl acetate (**6**)[d]	5.4	[f]	[f]	4.4	2.0	−12.5
Tri-*O*-benzoyl-β-D-xylopyranosyl acetate (**7**)	5.6	7.1	6.8	4.1	7.0	−12.3
Tri-*O*-benzoyl-α-D-lyxopyranosyl acetate (**8**)	3.1	3.2	9.1	4.5	9.0	−11.4

[a]Data taken from spectra measured at 100 MHz at a sweep width of 100 Hz. [b]Coupling constants calculated by ABX analysis. [c]The proton on C-5 giving the higher field signal is designated H-5'. [d]In chloroform-*d*. [e]$J_{2,4} = 0.7$ Hz. [f]First-order couplings not observed.

For each of the mixed esters (**1**–**8**) in acetone-d_6 at 31°, the n.m.r. spectral method of averaging of spin coupling[11] was used, by procedures already detailed[12], to determine the proportions of the *1C*(D) and *C1*(D) conformers present at equilibrium. Chloroform-*d* was used as the solvent with compounds **2** and **6** in order to obtain spectra easily interpreted.

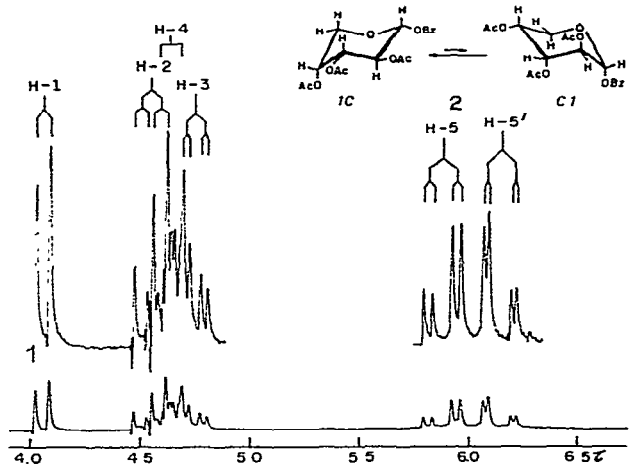


Fig. 1. Partial n.m.r. spectrum of tri-O-acetyl-α-D-arabinopyranosyl benzoate (2) in chloroform-d, at 100 MHz.

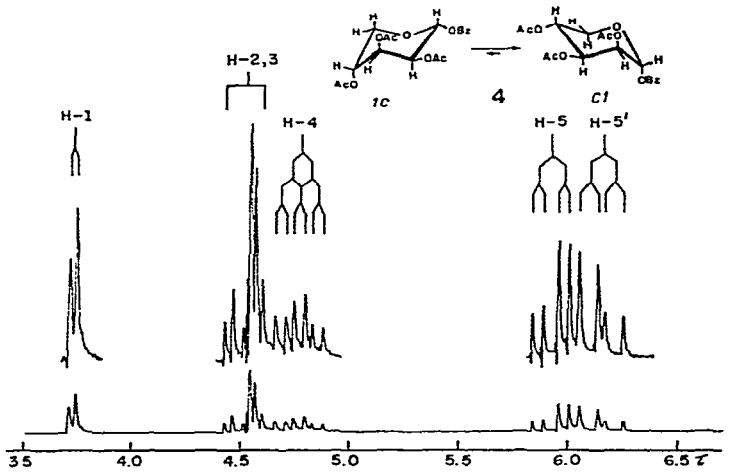


Fig. 2. Partial n.m.r. spectrum of tri-O-acetyl-α-D-lyxopyranosyl benzoate (4) in acetone-d_6, at 100 MHz.

Analysis of the signals of H-4 and the two protons at C-5 as ABX spin-systems[10] gave $J_{4,5}$ and $J_{4,5'}$ values for the peracetylated aldopentopyranosyl benzoates (**1**–**4**) and perbenzoylated aldopentopyranosyl acetates (**5**–**8**) that represent weighted time-averages for the two chair conformers in rapid equilibrium. Conformational

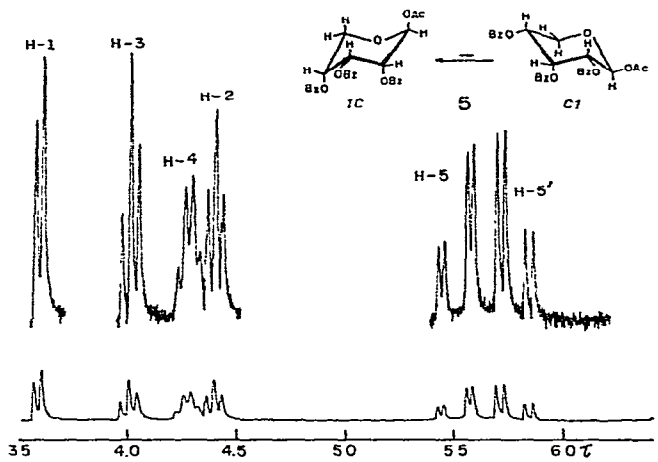


Fig. 3. Partial n.m.r. spectrum of tri-*O*-benzoyl-β-D-ribopyranosyl acetate (**5**) in acetone-d_6, at 100 MHz.

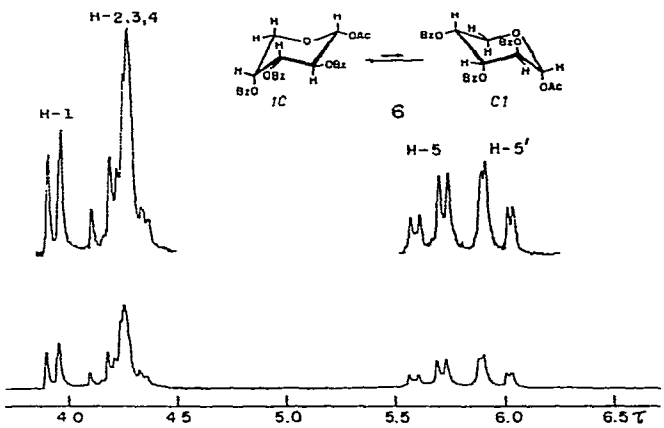


Fig. 4. Partial n.m.r. spectrum of tri-*O*-benzoyl-α-D-arabinopyranosyl acetate (**6**) in chloroform-*d*, at 100 MHz.

populations at 31° were determined from the observed coupling of H-4 with the *trans*-disposed proton at C-5, taken in conjunction with values for $J_{4e,5e}$ and $J_{4a,5a}$ that had been obtained from model compounds. The $J_{4,5a}$ value for α-D-xylopyranose tetraacetate (11.6 Hz)[2] was taken as the limiting magnitude of $J_{4a,5a}$ for each peracetylated aldopentopyranosyl benzoate, and the $J_{4,5a}$ value for α-D-xylopyranose tetrabenzoate (11.8 Hz)[2] as the limiting magnitude of $J_{4a,5a}$ for each perbenzoylated aldopentopyranosyl acetate. The model compounds chosen for obtaining $J_{4e,5e}$ were β-D-arabinopyranose tetraacetate and tetrabenzoate, respectively. The $J_{4,5'}$ values for both compounds decreased to a limit of 1.5 Hz at low temperatures[2], and this value was used throughout as the magnitude of $J_{4e,5e}$ for each of the eight mixed

esters. From the conformational populations determined from the spin-coupling data, the equilibrium constants (K) and values for free-energy differences ($\Delta G°$) for the $1C(D) \rightleftarrows C1(D)$ equilibria given in Table III were calculated. The limits of accuracy

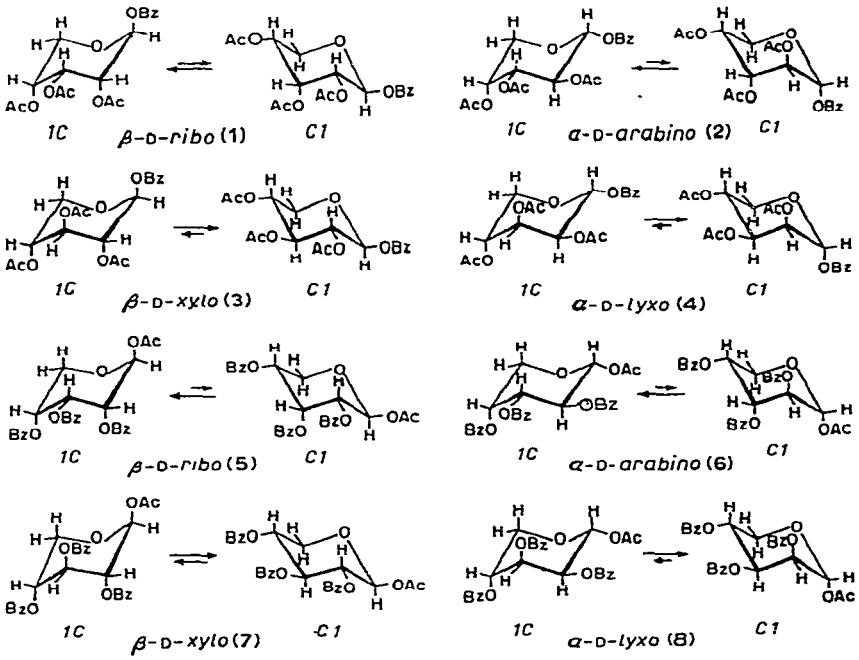


TABLE III

CONFORMATIONAL EQUILIBRIA OF 1,2-*trans* PERACETYLATED ALDOPENTOPYRANOSYL BENZOATES AND PERBENZOYLATED ALDOPENTOPYRANOSYL ACETATES

Compound	*Equilibrium data*			$\Delta G°_{31}$ (*kcal.mole*$^{-1}$) *for* 1C(D)⇄C1(D)
	% C1	% 1C	K = C1/1C	
Tri-*O*-acetyl-β-D-ribopyranosyl benzoate (**1**)	44	56	0.77	+0.16 ±0.28
Tri-*O*-acetyl-α-D-arabinopyranosyl benzoate (**2**)[a]	27	73	0.36	+0.62 ±0.31
Tri-*O*-acetyl-β-D-xylopyranosyl benzoate (**3**)	61	39	1.6	−0.28 ±0.27
Tri-*O*-acetyl-α-D-lyxopyranosyl benzoate (**4**)	72	28	2.6	−0.58 ±0.30
Tri-*O*-benzoyl-β-D-ribopyranosyl acetate (**5**)	22	78	0.29	+0.76 ±0.32
Tri-*O*-benzoyl-α-D-arabinopyranosyl acetate (**6**)[a]	28	72	0.39	+0.57 ±0.29
Tri-*O*-benzoyl-β-D-xylopyranosyl acetate (**7**)	53	47	1.1	−0.08 ±0.26
Tri-*O*-benzoyl-α-D-lyxopyranosyl acetate (**8**)	73	27	2.7	−0.60 ±0.29

[a]In chloroform-*d*.

for the calculations were determined from the uncertainty of ±0.1 Hz in the experimental values of the time-averaged couplings, in conjunction with a conservative estimate (±0.5 Hz) of the extent to which the "model" coupling-values actually differ from the true couplings for the separate conformers of each compound.

RESULTS AND DISCUSSION

Influence of substitution and configuration on the relative axial-directing effects of the acetoxy and benzoyloxy groups. — From an inspection of the conformational data given in Table III for the four tri-*O*-acetylaldopentopyranosyl benzoates (**1–4**) and the four tri-*O*-benzoylaldopentopyranosyl acetates (**5–8**), and the data previously reported[2] for the D-aldopentopyranose tetraacetates and tetrabenzoates, it is evident that the strength of the axial-directing effects of the acetoxy and benzoyloxy groups depends on the total stereochemistry of the derivative. In the β-D-*ribo* series, the axial-directing influence of the anomeric benzoyloxy group is very similar to that of the acetoxy group. Thus, β-D-ribopyranose tetraacetate[2] and tri-*O*-acetyl-β-D-ribopyranosyl benzoate (**1**) have almost the same conformational populations, and the same is true for β-D-ribopyranose tetrabenzoate[2] and tri-*O*-benzoyl-β-D-ribopyranosyl acetate (**5**). The strength of the axial-directing effects of the two groups is also very similar in the α-D-*lyxo* series, where the proportion at equilibrium of the *C1*(D) conformer for α-D-lyxopyranose tetraacetate[2] is nearly the same as that for tri-*O*-acetyl-α-D-lyxopyranosyl benzoate (**4**).

In the β-D-*xylo* and α-D-*arabino* series, however, the axial-directing influence of the benzoyloxy group appears to be larger than that of the acetoxy group. Thus, tri-*O*-acetyl-β-D-xylopyranosyl benzoate (**3**) has a greater proportion of the *1C*(D) conformer (axial C-1 substituent) at equilibrium (39%) than does β-D-xylopyranose tetraacetate[2] (28%). Similarly, the proportion of the *C1*(D) conformer (axial C-1 substituent) is greater for tri-*O*-acetyl-α-D-arabinopyranosyl benzoate (**2**) (27%) than for α-D-arabinopyranose tetraacetate[2] (21%). The difference in the relative strengths of the axial-directing influence of the acetoxy and benzoyloxy groups in the β-D-*xylo* and α-D-*arabino* series is a function of the nature of the substituents at C-2, C-3, and C-4. In the β-D-*xylo* series, the axial-directing influence of the benzoyloxy group is 0.3 kcal.mole^{-1} larger than that of the acetoxy group in the 2,3,4-triacetates, but only 0.1 kcal.mole^{-1} larger in the 2,3,4-tribenzoates. In the α-D-*arabino* series, the axial-directing influence of the anomeric benzoyloxy group is larger than that of the acetoxy group by 0.2 kcal.mole^{-1} when acetate groups are present at the other three ring positions, and by 0.1 kcal. mole^{-1} when benzoate groups are present.

It appears, therefore, that the relative strengths of the axial-directing influence of the acetoxy and benzoyloxy groups depend on whether or not the axial C-1 substituent has a *syn*-axial group at C-3. If such a *syn*-diaxial arrangement is present, as in the β-D-*xylo* and α-D-*arabino* configurations, the axial-directing influence of the anomeric benzoyloxy group is stronger than that of the acetoxy group, with the difference being larger when acetate groups are present at C-2, C-3, and C-4. On the other hand, if the axial C-1 substituent does not have a *syn*-axial group at C-3, as in the β-D-*ribo* and α-D-*lyxo* configurations, the axial-directing influences of the two groups are approximately the same.

The axial-directing influence of a polar substituent at C-1 is not independent of the substituents on O-2, O-3, and O-4. In the β-D-*ribo* series, the axial-directing

influence of the acetoxy or benzoyloxy group in the 2,3,4-tribenzoates is ~0.6 kcal. mole^{-1} larger than in the 2,3,4-triacetates. Thus, β-D-ribopyranose tetrabenzoate has substantially more of the *1C*(D) conformer at equilibrium (77%) than does tri-*O*-acetyl-β-D-ribopyranosyl benzoate (**1**) (56%). Changing the 2,3,4-substituents from acetates to benzoates in the α-D-*lyxo* series causes a negligible change (0.05 kcal. mole^{-1}) in the axial-directing influence of the acetoxy and benzoyloxy groups. In the β-D-*xylo* series, the more electronegative benzoate groups also enhance the axial-directing influence of the anomeric substituent, but that of the acetoxy group to a greater extent than that of the benzoyloxy group. Thus, the free-energy differences for β-D-xylopyranose tetraacetate[2] and tri-*O*-benzoyl-β-D-xylopyranosyl acetate (**7**) differ by 0.5 kcal.mole^{-1}, but those for β-D-xylopyranose tetrabenzoate[2] and tri-*O*-acetyl-β-D-xylopyranosyl benzoate (**3**) differ by only ~0.3 kcal.mole^{-1}. A similar effect is observed in the α-D-*arabino* series, where the axial-directing influence of the acetoxy group is enhanced by 0.24 kcal.mole^{-1} for the 2,3,4-tribenzoates as compared with the triacetates, but the corresponding enhancement for the benzoyloxy group is only 0.1 kcal.mole^{-1}. Hence, in the β-D-*ribo* and α-D-*lyxo* series, in which the axial C-1 substituent does not have a *syn*-axial group at C-3, the axial-directing influences of the two groups are affected similarly by replacing the acetate groups at C-2, C-3, and C-4 with benzoate groups. In contrast, in the β-D-*xylo* and α-D-*arabino* series, where an axial C-1 substituent has a *syn*-axial group at C-3, the axial-directing influences of the two groups at C-1 are affected differently, with that of the acetoxy group being the more strongly augmented by replacing the acetate groups at C-2, C-3, and C-4 by benzoate groups.

In the β-D-*ribo* and β-D-*xylo* series, the axial-directing effects of the polar anomeric substituents are more strongly enhanced by replacing acetate by benzoate groups at C-2, C-3, and C-4 than they are in the α-D-*arabino* and α-D-*lyxo* series. The stronger influence observed in the β-D-*ribo* and β-*xylo* series may be correlated with the *syn*-diaxial disposition of O-2 and O-4 in the conformation having the C-1 substituent axial; either a decreased repulsive interaction or an attractive interaction between *syn*-diaxial benzoyloxy groups at C-2 and C-4 might be involved.

Conformational equilibrium and its temperature dependence. — It was previously reported[2] that the conformational equilibria of β-D-xylopyranose tetraacetate and tetrabenzoate are affected differently by a change in the temperature. For the tetraacetate, the proportion of the all-equatorial *C1*(D) conformer increases with a decrease in the temperature, whereas, for the tetrabenzoate, the proportion of the alternative, all-axial *1C*(D) conformer increases with a lowering of the temperature. The shifts in the equilibrium positions were detected by changes in the vicinal spin-couplings as the temperature was decreased.

The temperature dependence of the conformational equilibria for the two β-D-*xylo* mixed esters (**3** and **7**) has now been investigated, with the aim of arriving at a better understanding of the factors that control conformational stability. For tri-*O*-acetyl-β-D-xylopyranosyl benzoate (**3**) and tri-*O*-benzoyl-β-D-xylopyranosyl acetate (**7**) in acetone-d_6, a decrease in the temperature resulted in an increase in the

values of the vicinal spin-couplings, indicating an increase in the equilibrium proportion of the *C1*(D) conformer for both derivatives, thus indicating a negative enthalpy difference ($\Delta H°$) for the *1C*(D) $\rightleftarrows$ *C1*(D) equilibrium. No "conformational freeze-out" was observed for either compound at low temperatures (−85°). The change in the conformational populations of the mixed esters was in the same direction as that observed for the tetraacetate, and opposite from that for the tetrabenzoate. Hence, changing the 2,3,4-substituents from acetates to benzoates to give **7**, or changing the C-1 substituent from acetate to benzoate to give **3**, is not sufficient to reverse the sign of the enthalpy difference observed for the tetraacetate between the two chair conformers. The *C1*(D) conformer of **3**, **7**, and the tetraacetate has the lower enthalpy. The reversal in sign occurs in the fully benzoylated β-D-xylopyranose derivative, for which the *1C*(D) conformation has the lower enthalpy.

In the β-D-*ribo* series, the shifts in the conformational population with temperature for the mixed esters were in the same direction as those observed for the tetraacetate and tetrabenzoate.[2] Thus, there was detected a decrease in the $J_{1,2}$ and the two $J_{4,5}$ couplings upon lowering the temperature for both tri-*O*-acetyl-β-D-ribopyranosyl benzoate (**1**) and tri-*O*-benzoyl-β-D-ribopyranosyl acetate (**5**) in acetone-d_6, indicating a shift in the equilibrium position toward the *1C*(D) conformer. No "conformational freeze-out" was observed for **5** at low temperature. It was, however, expected that, as the equilibrium constants for **1** and β-D-ribopyranose tetraacetate are very similar, **1** would yield a "freeze-out", as had previously been observed[12,13] for the tetraacetate. Although additional signals appeared in the n.m.r. spectrum of **1** in acetone-d_6 at low temperature (−85°), signifying a "freeze-out" of the equilibrium, the insufficient spectral dispersion at 100 MHz and the excessive line-broadening did not permit assignment of individual peaks that would have enabled calculation of the equilibrium constant and rate of conformational inversion.

Observation on chemical shifts. — From a study of the n.m.r. spectra of acetylated 1-*O*-acyl-D-glucopyranoses, Pravdić and Keglević[14] observed that, in derivatives containing an aryl- or indolyl-acetyl grouping ($ArCH_2CO$-) at O-1, the signal of the 2-acetoxy group appeared at unusually high field (τ 8.18–8.43). However, in 1-*O*-aroyl derivatives, where the carbonyl group is linked directly to the aromatic ring, no significant shift of any acetoxy-group signal was detected. The latter observation was attributed to the greater steric difficulty in aligning all of the acetoxy protons in the same shielding region above the aromatic ring. The tri-*O*-acetylaldopentopyranosyl benzoates (**1**–**4**) and the tri-*O*-benzoylated aldopentopyranosyl acetates (**5**–**8**) allowed examination of the effect of a benzoyloxy group on the chemical shift (in acetone-d_6 or chloroform-*d*) of an adjacent acetoxy group. As was noted by Pravdić and Keglević, the 1-*O*-benzoyl group did not cause any noticeable shift in the signal positions of the acetoxy group at the other three ring-positions. Similarly, the field-position of the signal of the C-1 acetoxy group was not noticeably affected by benzoyloxy groups at C-2, C-3, and C-4.

EXPERIMENTAL

General. — Evaporations were performed below 50° under diminished pressure. Melting points are uncorrected. Specific rotations were determined in a 1-dm, narrow-bore polarimeter tube. Microanalyses were made by W. N. Rond. T.l.c. was conducted with 0.25-mm layers of Silica Gel G (E. Merck, Darmstadt, Germany), activated at 120°, as the adsorbent, and sulfuric acid as the indicator. Column chromatography was performed with Silica Gel (7734, Merck) as the adsorbent, with 1 g of mixture to be separated per 30 g of adsorbent, and the compounds were eluted with the solvents specified.

N.m.r. spectra. — Spectra were recorded at 100 MHz with a Varian HA-100 n.m.r. spectrometer, under the general conditions specified in Ref. 3.

2,3,4-Tri-O-acetyl-β-D-ribopyranosyl benzoate (**1**). — To a solution of tri-*O*-acetyl-β-D-ribopyranosyl bromide[15] (1.0 g, 2.9 mmoles) in acetonitrile (10 ml) was added silver benzoate (0.70 g, 3.1 mmoles). The mixture was stirred in the dark at room temperature for 1 h, and then the silver salts were removed by filtration through a Celite pad, and the filtrate was evaporated. (Up to this point, the procedure was used, with minor modifications, for each of the products **1**–**8**). The resultant syrup was dissolved in the minimal volume of dichloromethane, and the solution was passed through a column of silica gel. Ether–dichloromethane (1:3) was used as the eluant, to separate the main product from a slower-moving component (probably a decomposition product of the bromide). The fractions containing the faster-moving component were concentrated to an amorphous glass, which crystallized from 95% ethanol to give **1**; yield 0.90 g (80%); m.p. 72–73°, $[\alpha]_D^{22}$ −73.2° (*c* 1.07, chloroform); R_F 0.75 (5:1 dichloromethane–ether); λ_{max}^{KBr} 5.73 (C=O), 6.24, 6.91, 7.30, 8.13, 8.74, 9.76, 10.37, 11.19, and 14.06 μm (aryl).

Anal. Calc. for $C_{18}H_{20}O_9$: C, 56.84; H, 5.30. Found: C, 57.09; H, 5.21.

2,3,4-Tri-O-acetyl-α-D-arabinopyranosyl benzoate (**2**). — Tri-O-acetyl-β-D-arabinopyranosyl bromide[16] (1.0 g, 2.9 mmoles) in acetonitrile (15 ml) reacted with silver benzoate (0.70 g, 3.1 mmoles), by the procedure used for **1**, to give a white solid, which was recrystallized from 95% ethanol to give **2**; yield 0.91 g (81%); m.p. 153°; $[\alpha]_D^{26}$ +12.2° (*c* 1.26, chloroform); R_F 0.81 (5:1 dichloromethane–ether); λ_{max}^{KBr} 5.74 (C=O) 6.24, 6.88, 7.29, 8.16, 9.16, 9.40, 10.36, 11.44, 12.36, and 13.96 μm (aryl).

Anal. Calc. for $C_{18}H_{20}O_9$: C, 56.84; H, 5.30. Found: C, 57.03; H, 5.36.

2,3,4-Tri-O-acetyl-β-D-xylopyranosyl benzoate (**3**). — Tri-*O*-acetyl-α-D-xylopyranosyl bromide[17] (1.6 g, 4.7 mmoles) in acetonitrile (15 ml) reacted with silver benzoate (1.1 g, 4.8 mmoles) during 30 min, by the procedure used for **1**, to give a white solid, which was recrystallized from anhydrous ether to give **3**; yield 1.5 g (85%); m.p. 147–148°, $[\alpha]_D^{19}$ −68.2° (*c* 1.16, chloroform) [lit.[8] m.p. 147–147.5°; $[\alpha]_D^{27}$ −70.3° (*c* 1.58, chloroform)]; R_F 0.83 (5:1 dichloromethane–ether); λ_{max}^{KBr} 5.70 (C=O), 6.24, 7.25, 8.12, 9.18, 9.41, 11.04, 11.36, 14.07 (aryl), and 14.29 μm (aryl).

Anal. Calc. for $C_{18}H_{20}O_9$: C, 56.84; H, 5.30. Found: C, 56.64; H, 5.16.

2,3,4-Tri-O-acetyl-α-D-lyxopyranosyl benzoate (**4**). — Tri-*O*-acetyl-α-D-lyxopyranosyl bromide[3] (1.0 g, 2.9 mmoles) in acetonitrile (15 ml) reacted with silver benzoate (0.70 g, 3.1 mmoles), by the procedure used for **1**, to give a thick syrup, which was crystallized from anhydrous ether. Recrystallization from ether gave **4**; yield 0.93 g (83%); m.p. 90–91°, $[\alpha]_D^{20}$ +52.7° (*c* 1.09, chloroform); R_F 0.80 (5:1 dichloromethane–ether); λ_{max}^{KBr} 5.74 (C=O), 6.24, 7.33, 8.13, 8.67, 9.15, 9.75, 10.20, 11.13, 11.58, and 14.06 μm (aryl).

Anal. Calc. for $C_{18}H_{20}O_9$: C, 56.84; H, 5.30. Found: C, 56.85; H, 5.54.

2,3,4-Tri-O-benzoyl-β-D-ribopyranosyl acetate (**5**). — Tri-*O*-benzoyl-β-D-ribopyranosyl bromide[18] (1.3 g, 2.5 mmoles) in benzene (15 ml) reacted with silver acetate (0.50 g, 3.0 mmoles) during 2 h, by the procedure used for **1**, to give a syrup; this was dissolved in the minimal volume of benzene and the solution was passed through a column of silica gel. Ether–benzene (1:9) was used as the eluant to separate the main product from a slower-moving component (probably a decomposition product of the bromide). The faster-moving component (**5**) was obtained as an amorphous glass; yield 0.94 g (75%); $[\alpha]_D^{22}$ −72.3° (*c* 1.05, chloroform); R_F 0.43 (9:1 benzene–ether); λ_{max}^{KBr} 5.65 (C=O), 5.77 (C=O), 6.89, 7.34, 7.61, 8.16, 9.32, 9.74, 10.41, 12.44, and 14.14 μm (aryl).

Anal. Calc. for $C_{28}H_{24}O_9$: C, 66.66; H, 4.80. Found: C, 66.63; H, 4.89.

2,3,4-Tri-O-benzoyl-α-D-arabinopyranosyl acetate (**6**). — Tri-*O*-benzoyl-β-D-arabinopyranosyl bromide[19] (2.9 g, 5.5 mmoles) in acetonitrile (25 ml) reacted with silver acetate (1.0 g, 6.0 mmoles) during 1.5 h, by the procedure used for **1**, to give a white solid; this was recrystallized once from 95% ethanol and twice from anhydrous ether to give **6**; yield 2.2 g (79%); m.p. 141°, $[\alpha]_D^{22}$ −192.9° (*c* 1.19, chloroform); R_F 0.50 (9:1 benzene–ether); λ_{max}^{KBr} 5.61 (C=O), 5.76 (C=O), 6.89, 7.93, 8.17, 9.13, 9.34, 9.70, and 14.15 μm (aryl).

Anal. Calc. for $C_{28}H_{24}O_9$: C, 66.66; H, 4.80. Found: C, 66.90; H, 4.77.

2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl acetate (**7**). — Tri-*O*-benzoyl-α-D-xylopyranosyl bromide[20] (1.8 g, 3.4 mmoles) in acetonitrile (20 ml) reacted with silver acetate (0.60 g, 3.6 mmoles) during 2 h, by the procedure used for **1**, to give a syrup which was crystallized from carbon tetrachloride–pentane. Two recrystallizations from anhydrous ether gave **7**; yield 1.3 g (77%); m.p. 125–126°; $[\alpha]_{365}^{21}$ +25.0°, $[\alpha]_D^{21}$ 0 ±0.5° (*c* 1.08, chloroform); R_F 0.56 (9:1 benzene–ether); λ_{max}^{KBr} 5.74 (C=O), 6.90, 7.95, 8.20, 8.58, 9.36, 9.72, 9.88, 10.44, 11.54, 12.11, and 14.11 μm (aryl).

Anal. Calc. for $C_{28}H_{24}O_9$: C, 66.66; H, 4.80. Found: C, 66.56; H, 4.81.

2,3,4-Tri-O-benzoyl-α-D-lyxopyranosyl acetate (**8**). — Tri-*O*-benzoyl-α-D-lyxopyranosyl bromide[21] (1.7 g, 3.2 mmoles) in acetonitrile (20 ml) reacted with silver acetate (0.60 g, 3.6 mmoles), by the procedure used for **1**, to give a syrup; this was dissolved in the minimal volume of benzene and the solution was passed through a column of silica gel. Ether–benzene (1:9) was used as the eluant, to separate the main product from a slower-moving component (probably a decomposition product of the bromide). The faster-moving component (**8**) was obtained as an amorphous glass; yield 1.2 g (71%); $[\alpha]_D^{20}$ −115.3° (*c* 0.703, chloroform); R_F 0.54 (9:1 benzene–

ether); λ_{max}^{KBr} 5.66 (C=O), 5.77 (C=O), 6.23, 6.89, 7.59, 7.93, 9.35, 9.97, 10.31, and 14.12 μm (aryl).

Anal. Calc. for $C_{28}H_{24}O_9$: C, 66.66; H, 4.80. Found: C, 66.87; H, 5.01.

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