Carbohydrate Research, 88 (1981) 277–289
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

CHEMICAL AND PHYSICAL STUDIES ON OLIGOSACCHARIDES. ISOLATION, CONFIGURATIONS, AND CONFORMATIONS OF THE PER-*O*-ACETYL-*O*-β-D-GLUCOPYRANOSYL-(1→3)-D-ARABINOSES

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(Received July 21st, 1980; accepted for publication, August 8th, 1980)

ABSTRACT

The reaction of octa-*O*-acetylcellobiononitrile with sodium methoxide, and acetylation of the resulting mixture, afforded the anomeric peracetates of *O*-β-D-glucopyranosyl-(1→3)-D-arabinopyranose and *O*-β-D-glucopyranosyl-(1→3)-D-arabinofuranose, which were isolated by fractional recrystallization. Their structures, anomeric configurations, and conformations were studied by chemical, optical, and spectroscopic methods.

INTRODUCTION

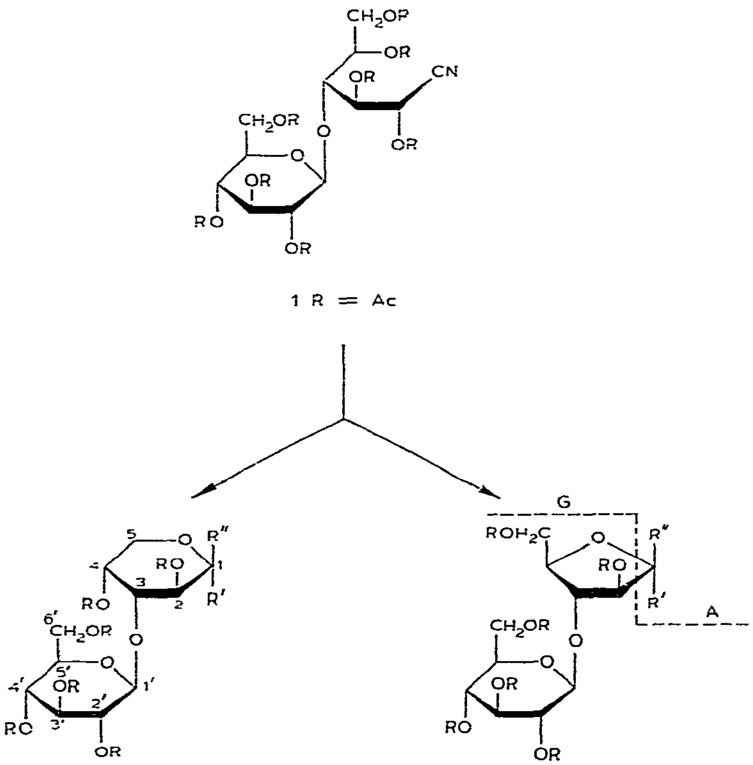
The reaction of octa-*O*-acetylcellobiononitrile (**1**) with sodium methoxide gave a mixture of glucosyl-arabinoses, and these were separated as their peracetates by fractional recrystallization. The proposed structures and physical data for these acetates are shown in Scheme 1.

By degradation of **1** with sodium methoxide, and subsequent acetylation, Zemplén[1] isolated compound **2** in a yield of 33%. In the same paper, two other acetates were also described, although not structurally defined, whose physical data differed from those of the acetates described here. One of them, "heptaacetyl-glycoarabinose B" (m.p. 157–161°, $[\alpha]_D$ −50.2°)[1] could be considered to be an unresolved mixture. Compound **2** has been also isolated[2] after ultraviolet irradiation of wood pulp, and chromatographic fractionation, and acetylation, of the products.

RESULTS AND DISCUSSION

From the chemical point of view, it has now been observed that compounds **2** and **4** are readily interconverted by anomerization reagents, whereas compounds **3** and **5** are extensively decomposed, and not unambiguously interconverted.

A β-pyranose anomer can be obtained by heating the corresponding α-pyranose with acetic anhydride–acetic acid and a catalytic amount of sulfuric acid[3]. When **2** was treated with this mixture, compound **4** was obtained in 50% yield as the only



1 R = Ac

2 R = R′ = OAc, R″ = H (m.p. 196°, $[\alpha]_D$ −16.9°)

4 R′ = H, R = R″ = OAc (m.p. 139°, $[\alpha]_D$ −85.4°)

3 R′ = H, R = R″ = OAc (m.p. 151°, $[\alpha]_D$ −36.0°)

5 R = R′ = OAc, R″ = H (m.p. 127°, $[\alpha]_D$ −7.1°)

Scheme 1

disaccharide acetate produced in the reaction. On the other hand, reaction of **4** with acetic anhydride–zinc chloride, commonly used to convert a β-pyranose into the corresponding α anomer[4], gave a mixture of **2** and **4**. Treatment of compound **3** with this reagent led to inconclusive results, acetates **2** and **4** not being detected. In this case, this technique also produced extensive acetolysis and degradation products. The reaction of **5** with the acetic anhydride–acetic acid–sulfuric acid reagent gave 50% of the starting material and acetolysis products.

These experiments suggest an anomeric pentopyranose relationship between compounds **2** and **4**, and, on this basis, considering the respective rotatory powers, the α anomeric configuration could be assigned to **2**, and the β to **4**.

Optical correlations. — Some considerations will now be undertaken concerning the possibility of extending the optical rotatory method (previously applied to glycosides[5,6], disaccharides[7–9], and nonreducing sugar acetates[9]) in order to support the proposed anomeric configurations of these reducing-sugar acetates. According to that procedure, the molar rotation of any glycoside possessing an optically active aglycon may be calculated by summation of the molar rotations of the two portions of the molecule. In the present case, summation of the molar rotation of methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside[10] (−6769°) and the respective values of the anomeric pair of 1,2,4-tri-*O*-acetyl-3-*O*-methyl-D-arabinopyranoses would give the calculated rotatory powers of **2** and **4**. The lack of literature data on the 3-*O*-methyl-D-arabinose acetates precluded rigorous use of the method; however, the results obtained by using the data corresponding to the anomeric tetra-*O*-acetyl-D-arabinopyranoses (−13,928° for the α-D form[11] and −46,587° for the *β*-D, taken from that in the L series[12], in chloroform) showed acceptable congruence with the experimental values. The experimental rotatory powers of **2** and **4** were −16.9 and −85.4°, respectively, whereas the values calculated were −34.1 and −88.0°, respectively*.

On the other hand, independent verification (see later) that compounds **3** and **5** constitute an anomeric pair of pentofuranoses indirectly supports the relationship between **2** and **4**.

For the acetates **3** and **5**, the foregoing calculations could not be applied, as the arabinofuranose acetates have not previously been described in the literature as anomerically pure compounds[13], but a useful correlation can be made by considering the rotatory powers of the peracetylated *β* ($[\alpha]_D$ −14.4°) and α ($[\alpha]_D$ +23.1°) anomers of *β*-D-glucopyranosyl-(1→5)-D-arabinofuranose[14], whose structure in the pentose portion derives unambiguously from the alkaline degradation of hepta-*O*-acetylgentiobiononitrile. If the difference between **3** and the (1→5)-*β* derivative, and between **5** and the (1→5)-α compound lies only in the point of attachment of the hexosyl group, the difference in rotatory power between the two pairs of analogous anomers, being affected by the same structural difference, would be approximately the same. The data, 21.6° for the *β* pair, and 30.2° for the α, show acceptable concordance.

A second, optical, approach to the structure of this pair of anomers is by calculation of the molar rotation A of the anomeric, non-glycosidically linked, carbon atom, and comparison with the analogous values obtained from unambiguously ascertained structures.

On the basis of the Hudson rules, the rotatory power of **3** and **5** may be considered to be the algebraic sum of the G and A portions[15] (indicated by dotted lines in Scheme 1) of the molecule. Thus, the molar rotation of **3** will be $M_3 = G - A$: $(-36.0 \times 606 = -2{,}816°)$, and that of **5**: $M_5 = G + A$: $(-7.1 \times 606 = -4{,}302°)$. The difference $[M]_5 - [M]_3 = 2\,A$; therefore, $A = +8{,}757°$. In the same way,

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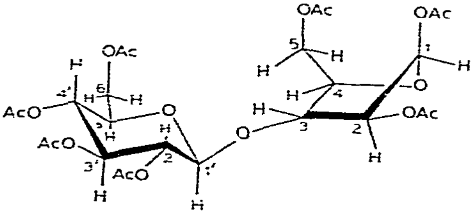
*This approach rests upon the assumptions that the changing of R in one -OR ring substituent, or a change in the point of insertion of that substituent, involves only minor variations in the rotatory power, provided that the substituents at the anomeric carbon atom are excluded from this generalization. Such calculations for several, known, reducing-disaccharide peracetates gave good agreement with the corresponding, literature data.

for comparison purposes, the A value may be calculated for the anomeric pair of the aforementioned hepta-*O*-acetyl-β-D-glucopyranosyl-(1→5)-D-arabinofuranose[14] (A = +11,362°) and also for the hepta-*O*-acetyl-*O*-α-D-galactopyranosyl-(1→5)-D-arabinofuranose (unambiguously synthesized by degradation of octa-*O*-acetylmelibiononitrile[16]), which give A = +9,272°.

The same kind of calculations applied to **2** and **4** gave A = +20,595°.

N.m.r. studies. — The n.m.r. spectra of the four disaccharide acetates were measured at 100 MHz in deuteriochloroform with tetramethylsilane as the standard. The chemical shifts are given on the δ scale, and were obtained by analysis of the spectra on a first-order basis, unless otherwise stated.

In these spectra, three distinct regions may be observed, one of which is the acetyl-proton region at δ 2.00–2.20. The protons attached to the carbon atoms of the sugar residues give rise to two groups of signals. That appearing at fields higher than δ 4.7, comprising seven protons, arises from H-3, H-5', the methylene groups, and also H-1', which shows its resonance at the lower-field limit of this region (for numbering of the protons, see **6**). Resonances below δ 4.7, comprising six protons, may be assigned to the remaining methine protons, that of H-1 being the lowest-field signal of the spectra. Table I shows the chemical shifts of the peracetylated glucosylarabinopyranose anomers **2** and **4**, and glucosylarabinofuranose anomers **3** and **5**, at 100 MHz, in chloroform-*d*. Table II shows the values of the corresponding constants.



6

For the conformational analysis of the acetates herein described, use has been made of the equation and parameters previously reported[17], which take into account the angular dependence of the coupling constant and also the electronegativities of the substituents. In this way the dihedral angles between the vicinal protons of the sugar ring were calculated by using the observed coupling constants (see Table II), and the values are shown in Table III.

The spectra of the penta-*O*-acetyl-β-D-glucopyranosyl group show little variation for the four sugars. The value of 7 Hz for $J_{1',2'}$ agrees for a *trans*-diaxial relationship of H-1' and H-2'. At the highest field of the spectra, but below the acetyl-proton region, the four acetates show the H-5' multiplet (for compound **2**, it is partially superimposed on H-5b), whose irradiation allowed ascertaining of H-6'a and H-6'b and, at lower field, H-4'. The C-6' methylene group was the coupled AB part of an ABX system, and its n.m.r. parameters were obtained by ABX analysis[18], except in

TABLE I

^{1}H-N.M.R. CHEMICAL-SHIFTS (δ), AT 100 MHz, OF THE PERACETYLATED O-β-D-GLUCOPYRANOSYL-(1→3)-D-ARABINOSES IN $CDCl_3$

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5a*	*H-5b*[a]	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6'a*	*H-6'b*[a]
β-D-Glc*p*-(1→3)-													
α-D-Ara*p* (2)	5.73	5.22	4.04	~5.15	4.01	3.64	4.60	4.96	5.06–5.15		3.73	4.30	4.10
β-D-Ara*p* (4)	6.28	5.36	4.20	~5.10	3.96	3.81	4.64	5.01	5.10–5.30		3.74	4.32	4.14
β-D-Ara*f* (3)	6.36	5.34	4.06	5.16	3.88–4.44		4.68	← 4.90–5.35 →			3.72	4.40–4.10	
α-D-Ara*f* (5)	5.74	5.43	4.16	~5.10	4.66	3.97	4.62	← 5.10–5.30 →			3.70	4.31	4.15

[a]The protons on C-5 and C-6' giving the higher-field signal are designated H-b.

TABLE II

VALUES OF ^{1}H COUPLING-CONSTANTS (Hz) OF THE PERACETYLATED O-β-D-GLUCOPYRANOSYL-(1→3)-D-ARABINOSES

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$[a]	$J_{5a,5b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'a}$	$J_{5',6'b}$[a]	$J_{6'a,6'b}$
β-D-Glc*p*-(1→3)-													
α-D-Ara*p* (2)	4.5	7.0	3.0	6.5	3.5	−12	7.0	8.0	[b]	[b]	5.0	2.2	−12
β-D-Ara*p* (4)	3.0	9.5	4.0	2.8	4.0	−13	7.0	7.0	[b]	[b]	4.7	1.7	−12
β-D-Ara*f* (3)	4.5	6.5	3.0	[b]	[b]	[b]	7.0	[b]	[b]	7.5	[b]	[b]	[b]
α-D-Ara*f* (5)	4.0	2.5	4.0	3.0	4.0	−13	7.0	[b]	[b]	8.0	2.3	2.9	−12

[a]The protons on C-5 and C-6' giving the higher-field signal are designated H-b. [b]First-order couplings not observed.

TABLE III

CALCULATED DIHEDRAL ANGLES FOR THE PER-*O*-ACETYL-*O*-β-D-GLUCOPYRANOSYL-(1→3)-D-ARABINOSES

Compound	$\phi_{1,2}$	$\phi_{2,3}$	$\phi_{3,4}$	$\phi_{4,5a}$	$\phi_{4,5b}$	$\phi_{1',2'}$	$\phi_{2',3'}$	$\phi_{4',5'}$
β-D-Glc*p*-(1→3)-								
α-D-Ara*p* (2)	128	141	57	—	—	142	148	—
β-D-Ara*p* (4)	55	153	49	61	47	142	141	—
β-D-Ara*f* (3)	27	141	120	—	—	142	—	144
α-D-Ara*f* (5)	131	118	127	—	—	142	—	147

the case of **3**, in which both protons have the feature of a deceptively simple, ABX system.

The simultaneous decoupling of H-6'a and H-6'b collapses H-5' to a doublet, from which, in the case of compounds **3** and **5**, $J_{4',5'}$ (7.5 and 8 Hz, respectively) could be ascertained. On the other hand, irradiation of H-1' allowed, in the case of **2** and **4**, the ascertaining, on a first-order basis, approximate values for $J_{2',3'}$ of 8 and 7 Hz, respectively. Because H-3' was included in the low-field multiplet (δ 5.06–5.30) and near to H-2', the values for $J_{2',3'}$ are approximate, but their range for this pyranose portion of the molecule is diagnostic of a *trans*-diaxial relationship. The values of $J_{1',2'}$, $J_{2',3'}$, and $J_{4',5'}$ obtained separately for the four disaccharides, assuming that the ring of the hexose moiety does not change conformationally (as suggested by the identical $J_{1',2'}$ values for the four compounds) indicate a common $^4C_1$(D) conformation for that part of the molecule. The calculated dihedral angles (see Table III) suggest a more pronounced flattening, owing to steric compression, of the ideal $^4C_1$(D) conformation than that observed[17] with other such acetates.

The n.m.r. signals of the protons pertaining to the pentose moiety of the four acetates showed differences for each compound that will be considered separately, as follows.

Hepta-O-*acetyl-β*-D-*glucopyranosyl-(1→3)-β*-D-*arabinofuranose* (**3**). — In the spectrum of this isomer, H-1 appeared at δ 6.36, with $J_{1,2}$ 4.5 Hz. Comparison with the corresponding values for the α anomer **5** (δ 5.74, $J_{1,2}$ 4 Hz) shows that the coupling constants, as with other types of furanose derivatives[19], fail to distinguish between the anomers, but the lower-field resonance for the β anomer **3** agrees with a cis relationship of the C-1, C-2 substituents[20,21]. By irradiation of H-1, a pair of doublets at δ 5.34 (H-2) collapses to a doublet, $J_{2,3}$ 6.5 Hz. As with the other three isomers, H-3 resonates in the multiplet at the higher-field region, and is seen as a distinct pair of doublets. In that multiplet are, also, signals for H-5a, H-5b, H-6'a, and H-6'b, but their signals were not clearly assignable. The C-6' methylene group appeared as the AB portion of a deceptively simple, ABX system.

Hepta-O-*acetyl-β*-D-*glucopyranosyl-(1→3)-α*-D-*arabinofuranose* (**5**). — The higher-field resonance for H-1, relative to that of H-1 of the β-furanose anomer **3**, showed the known, shielding effect of a *cis*-acetoxyl substituent[19,20] on C-2. H-2 appears as a separate pair of doublets at lower field than for H-3, and the value $J_{2,3}$ 2.5 Hz indicates a more "gauche" relationship of H-2–H-3 than in 3. The rest of the coupling constants (see Table I) were determined with the aid of double-resonance experiments. The H-5a and H-5b signals (which, in 3 and 4, are strongly coupled) for this isomer appear as two well-separated pairs of doublets amenable to first-order analysis, H-5a being superimposed on H-1′ (see Fig. 1).

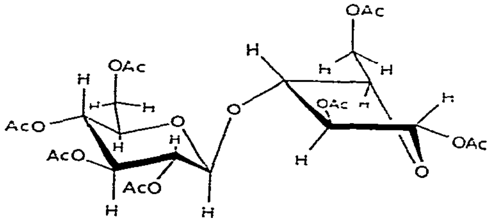
Some consideration can now be given to the conformation of the furanose isomers 3 and 5. The barrier for conformational inversion of a furanose ring could be considered in the range[22,23] of 12.6–16.8 kJ/mol (~3-4 kcal/mol), and this implies a fast, conformational inversion (on the n.m.r. time-scale) at room temperature. The 20 symmetrical conformations having a maximal puckering of the furanose ring are related[23,24] by the "pseudorotational cycle" which, by the influence of steric and polar interactions, would be populated preferably in limited segments.

On the other hand, because of the limited accuracy of the dihedral angles derived from vicinal coupling-constants, a range of dihedral separations (with ~20° of difference between extreme values) may be considered. In this sense, the figures shown in Table III for 3 and 5, derived from the coupling constants listed in Table II, should be regarded as mean reference-values from these ranges.

In the case of compound 3, comparison of the approximate, calculated angles with those estimated from Dreiding models for the conformations pertaining to the pseudorotational cycle allows discounting of those conformations at variance with the dihedral angles experimentally determined[24]. From the three separate evaluations for $\phi_{1,2}$, $\phi_{2,3}$, and $\phi_{3,4}$, a single overlap was observed, located in the region of ^{1}E (see 6), $^{1}T_{2}$, and E_{2} of the pseudorotational cycle.

From molecular models of 3, it was observed that these conformations tend to alleviate the eclipsed disposition of the acetoxyl groups on C-1 and C-2, and, to a certain extent, to maintain the bulky substituent on C-3 in a definitely equatorial disposition. The experimental n.m.r. data are thus congruent with the steric interactions observed.

Application of a similar procedure to compound 5 showed an overlapping segment corresponding to the E_{0} (see 7) and $^{1}T_{0}$ conformations. This puckering provides maximal staggering of all of the bulky substituents, and also tends to axialize that on C-4, thus achieving better separation from the substituent on C-3.



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Hepta-O-acetyl-O-β-D-glucopyranosyl-(1→3)-β-D-arabinopyranose (**4**). — The H-1 signal appeared at lower field than for the α-pyranose anomer **2**, suggesting an equatorial orientation[25] of this proton in the $^1C_4$(D) conformation. Irradiation of H-1 located H-2 at δ 5.36, which collapsed to a doublet, $J_{2,3}$ 9.5 Hz, showing the *trans*-diaxial relationship of H-2, H-3, whereas the value of $J_{3,4}$ (4 Hz) fits a gauche, axial–equatorial orientation of H-3, H-4. The n.m.r. parameters of H-5a and H-5b were obtained by an ABX analysis[18]. The $J_{5a,5b}$ geminal coupling of −13 Hz also supports the proposed conformation, because this value is congruent with the axial orientation of the acyloxy group on C-4 (antiparallel to H-5 axial), as has also been observed for a series of aldopyranose derivatives[26].

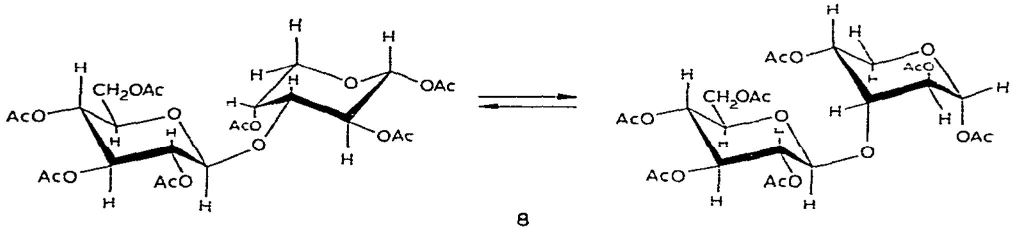
Hepta-O-acetyl-O-β-D-glucopyranosyl-(1→3)-α-D-arabinopyranose (**2**). — The H-1 atom resonates at higher field than that in **4**, suggesting an axial orientation in the $^1C_4$(D) conformation. The coupling constant for the H-2–H-3 dihedral angle (7 Hz) is reasonable for a *trans*-diaxial orientation of these protons, but this value, as well as that of $J_{1,2}$ (4.5 Hz), indicates some contribution of the $^4C_1$(D) conformation, or, alternatively, a certain degree of flattening of the $^1C_4$(D) conformer.

The angles listed in Table III for compound **2** could be interpreted, in the first instance, as corresponding to a favored, flattened, $^1C_4$(D) conformation in which H-4 would bisect the geminal, C-5 protons, the bulky substituent on C-3 being equatorially oriented. The alternative to an equilibrium with the $^4C_1$(D) conformation, which would have that C-3 substituent in the axial orientation, (this destabilizing factor being aggravated by a parallel, 1,3-interaction with the axial acetoxyl group on C-1) seems improbable. The flattening of the ring in the former conformer could thus be considered a compromise between two opposing tendencies; the anomeric effect, causing the acetoxyl group on C-1 to become axial, and, on the other hand, the equatorial-directing effect of the bulky substituent on C-3. The two opposing effects would result in quasi-axial[27] attachment of the bulky substituents.

However, this view is not supported by several pieces of evidence. Firstly, if the anomeric effect were so strong, the favored conformation for tetra-*O*-acetyl-α-D-arabinopyranose would be $^4C_1$(D), as the 3-acetoxyl group would not, on a steric basis, preclude a definite shift of the equilibrium towards this conformer, which has the 1-acetoxyl group in the axial orientation. However, studies conducted with this tetraacetate[11] showed that the favored conformation is $^1C_4$(D), with 79% of this form in the conformational equilibrium.

Secondly, the change observed in the geminal coupling-constant ($J_{5a,5b}$ −12 Hz) for compound **2**, as compared with that for **4** (−13 Hz), reflects an increased bisecting disposition[26] of the 4-acetoxyl group with regard to the methylene protons on C-5. This is also supported by the value of 6.5 Hz for $J_{4,5a}$, indicating a substantial contribution of the form having a *trans*-diaxial relationship of the two protons on C-4 and C-5. Consequently, in the case of compound **2**, other factors, probably emerging from polar, attractive forces between the C-1 and C-3 substituents, play a role, and the $^4C_1$(D) conformation, having these two substituents in the *syn*-

diaxial relationship favorable for full attractive interaction, in equilibrium with the $^{1}C_{4}$(D) conformation, as in **8**, would be highly probable.



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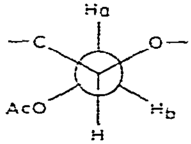
Assuming an equilibrium mixture of the $^{4}C_{1}$(D) and $^{1}C_{4}$(D) conformers for the pentopyranose residue of **2**, the conformational populations at room temperature were determined from the observed coupling-constants by application of the method of averaging of coupling constants[28,29]. For compound **2**, we calculated conformational populations from three coupling-constants ($J_{1,2}$, $J_{2,3}$, and $J_{4,5a}$), for which literature data are available as to limiting values of the vicinal coupling-constants, applicable to each chair conformation of the pentopyranose moiety as depicted in **8**. These were (in Hz): $J_{1a,2a}$ 7.5 (ref. 29), $J_{1e,2e}$ 1.0 (ref. 29), $J_{2e,3e}$ 3.0 (ref. 30), $J_{2a,3a}$ 10.25 (ref. 31), $J_{4e,5e}$ 1.5 (ref. 11), and $J_{4a,5a}$ 11.6 (ref. 11). The calculated percent of the $^{4}C_{1}$(D) form of the acetylated arabinopyranose portion of **2**, based on the individual J values, were: 47% from $J_{1,2}$, 45% from $J_{2,3}$, and 49% from $J_{4a,5a}$. These results are consistent, and support the presence of a mixture of the chair conformers.

The *β*-pyranose acetate **4** shows angles that fit well for a favored $^{1}C_{4}$(D) conformation of the pentopyranose portion. The determination of the percent of the $^{1}C_{4}$(D) conformer was performed with the $J_{2,3}$ and $J_{4a,5a}$ values observed, employing the corresponding, aforementioned, limiting values of vicinal coupling-constants used for **2**. Thus, from $J_{2,3}$, 89%, and from $J_{4a,5a}$, 76%, were calculated, which means an average of 82.5% of the $^{1}C_{4}$(D) form. With tetra-*O*-acetyl-*β*-D-arabinopyranose in acetone-d_6, 96% of the $^{1}C_{4}$(D) form, based on the $J_{4a,5a}$ value observed, was found[11].

The four acetates showed, as a general feature, the H-3 resonance at higher field than the rest of the protons of the pentose ring (excepting the methylene group in the pentopyranose residues of **2** and **4**, which resonates at higher field). This could be attributed to a shielding influence of the glycosyl group attached to O-3. An analogous effect was observed with furanose sugars[32] possessing methoxyl groups as substituents.

The orientation of the 5′-CH₂OAc group. — The 5′-CH_2OAc group in the four acetates can adopt various orientations by rotation around the exocyclic, C-5′–C-6′ bond. The same occurs with the 4-CH_2OAc group in the pentofuranose portion of **3** and **5**. We shall first consider the hexopyranosyl unit by the method of averaging of spin coupling[28,29], in the way previously discussed[17] for other derivatives of oligosaccharides.

The most important of the staggered rotamers contributing to the time-averaged spectrum are represented in **9**, **10**, and **11**.



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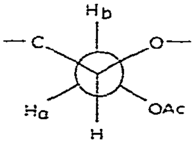

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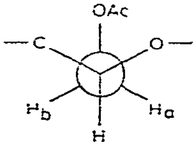

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The observed, vicinal coupling-constants, $J_{5',6'a}$ and $J_{5',6'b}$, allow the calculation of the mole fractions n_9, n_{10}, and n_{11} of the three rotamers for our acetates, according to the equations and limiting values of coupling constants previously proposed[17].

In this way, the rotameric, molar fractions for the 5'-CH_2OAc fragment in compounds **2**, **4** and **5** were, respectively: n_9, 0.04; 0.01; and 0.06; n_{10}, 0.36; 0.32; and 0.15; and n_{11}, 0.60; 0.67; and 0.79. These values are in close correspondence with those calculated for penta-*O*-acetyl-β-D-glucopyranose[17] (*i.e.*, n_9, 0.02; n_{10} 0.33; and n_{11}, 0.65).

Excluding n_{11}, because Ha and Hb make the same contribution to $J_{5',6'a}$ and $J_{5',6'b}$ through rotamer **11**, and as, for rotamers **9** and **10**, Ha and Hb were arbitrarily differentiated, the alternative, interchanging the n_9 and n_{10} values, is open to consideration. However, rotamer **9** is disfavored, owing to a parallel 1,3-interaction between the acetoxyl groups on C-4' and C-6', and this justifies the choosing of the small value for n_9. In formulas **6** and **7**, the favored orientation for the exocyclic grouping in the D-glucopyranosyl unit is depicted. The higher-field signal H-6'b would correspond to the proton anti-periplanar with the electronegative substituent O-5; this arrangement implies that the value of $J_{5',6'b}$ is lower than that of $J_{5',6'a}$. That signal would be at higher field, owing to a 1,3-diparallel, relative shielding of that proton by the acetoxyl substituents[32] on C-4.

Orientation of the 4-CH_2OAc group. — The same reasoning applied to the data for the acetylated D-arabinofuranose unit in **5**, led to the molar fractions n_9 0.13, n_{10} 0.26, and n_{11} 0.61 for the 4-CH_2OAc grouping. The alternative values of n_9 0.26 and n_{10} 0.13 are also possible, but would imply a higher degree of crowding, as the 5-acetoxyl group would interact closely with the hexosyl portion. Nevertheless, the preponderance of the rotamer having H-4 bisecting the methylene group at C-5, as depicted in **7**, is evident.

EXPERIMENTAL

General procedures. — T.l.c. was conducted on Silica Gel G (Merck) with 9:1 benzene–absolute ethanol as eluant, and with four consecutive developments. The spots were detected with iodine vapor or with alkaline hydroxylamine–ferric nitrate[34]. N.m.r. spectra (100 MHz) were recorded at 20–25° with a Varian XL-100 spectrometer, with tetramethylsilane as the internal reference-standard. Optical rotations were measured at 20–25° with a Perkin–Elmer 141 polarimeter.

Reaction of octa-O-acetylcellobiononitrile with sodium methoxide, and per-acetylation of the sugars obtained. — Octa-*O*-acetylcellobiononitrile[1] (**1**, 10 g) was dissolved in dry chloroform (26 mL) and, after cooling at 0°, a solution of sodium (0.5 g) in absolute methanol (25 mL) was added. The solution become viscous, and was kept for 30 min at room temperature with occasional stirring. After dilution with water (30 mL), the chloroform layer was decanted, and washed twice with water. The aqueous layers were combined, shaken with sulfonic resin Zeokarb 225 (H^+) until neutral, and after filtration, the filtrate was evaporated to a syrup (5.7 g) that was dissolved in 1 : 1 pyridine–acetic anhydride (400 mL) precooled to 0°. The mixture was kept for 96 h at 5°, poured onto crushed ice, and extracted with chloroform (4 × 200 mL), and the extracts were combined, dried (Na_2SO_4), and evaporated to a syrup that was treated as follows.

*Hepta-O-acetyl-O-β-*D*-glucopyranosyl-(1→3)-α-*D*-arabinopyranose* (**2**). — The syrup just obtained was dissolved in methanol, and **2** readily crystallized; 2.43 g (27.2% yield), m.p. 194–195°. Recrystallization from methanol gave rectangular plates that initially showed m.p. 161–162°, with simultaneous rearrangement to needles that finally melted at 196–197°, $[\alpha]_D$ −16.9° (*c* 0.98, $CHCl_3$); t.l.c. showed only one spot, R_F 0.67; lit.[1] m.p. 196°, $[\alpha]_D$ −16.9° ($CHCl_3$).

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.52; H, 5.61. Found: C, 49.80; H, 5.86.

*Hepta-O-acetyl-O-β-*D*-glucopyranosyl-(1→3)-β-*D*-arabinofuranose* (**3**). — After slow evaporation at room temperature. the methanolic mother liquor of **2** gave a second product (0.9 g), m.p. 132–144°, that t.l.c. demonstrated to be a mixture of **3** and **4**. Recrystallization from methanol gave 0.71 g (7.9%) of **3**, m.p. 154–155°, $[\alpha]_D$ −36.0° (*c* 0.5, $CHCl_3$); t.l.c. showed only one spot, R_F 0.72.

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.52: H, 5.61. Found: C, 49.89; H, 5.94.

*Hepta-O-acetyl-O-β-*D*-glucopyranosyl-(1→3)-β-*D*-arabinopyranose* (**4**). — After separation of compound **3** as just described, slow evaporation of the methanolic mother liquors afforded crystalline **4** (0.16 g, 1.78%) which, after recrystallization from methanol, had m.p. 139–140°, $[\alpha]_D$ −85.4° (*c* 0.14, $CHCl_3$): t.l.c. showed only one spot, R_F 0.62.

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.52; H, 5.61. Found: C, 49.72; H, 5.86.

*Hepta-O-acetyl-O-β-*D*-glucopyranosyl-(1→3)-α-*D*-arabinofuranose* (**5**). — The methanolic solution from which compounds **2**, **3**, and **4** had been obtained was evaporated to dryness, and the residue was dissolved in 2-propanol. Compound **5** crystallized as needles (2.85 g, 31.8%), m.p. 119–120°. Recrystallization from 2-propanol gave pure **5**, m.p. 127–128°, $[\alpha]_D$ −7.1° (*c* 0.4, $CHCl_3$); t.l.c. showed only one spot, R_F 0.64.

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.52; H, 5.61. Found: C, 49.83; H, 5.56.

Anomerizations with acetic anhydride–anhydrous zinc chloride. — (*a*). Compound **3** (20 mg) was dissolved in acetic anhydride (0.6 mL), and anhydrous zinc chloride (5 mg) was added. The mixture was heated in a boiling-water bath for 45 min (until a brown coloration begin to intensify markedly). The solution was diluted with water, and extracted with chloroform (4 × 5 mL). The extracts were combined, successively washed with saturated sodium hydrogencarbonate solution, and water, dried (Na_2SO_4), and evaporated; the residual syrup did not crystallize from methanol or 2-propanol, and, in t.l.c., showed one spot, R_F 0.72, coincident with that for the starting compound (**3**).

(*b*). Compound **4** was anomerized as described for **3**. Part of the starting product was recovered, and the mother liquors gave, in t.l.c., only two spots, R_F 0.62 (**4**) and 0.67 (**2**), coincident with those for pure samples thereof.

Anomerizations with acetic anhydride–acetic acid–sulfuric acid. — (*a*). Compound **2** (300 mg) was added to cooled, 1:1 acetic anhydride–glacial acetic acid (24 mL). After dissolution, concentrated sulfuric acid (two drops) was added, and the mixture was kept at 50°, the reaction being monitored by t.l.c. After 5 days, the solution was poured into chloroform, successively washed with saturated sodium hydrogencarbonate solution and water, dried (anhydrous sodium sulfate), and evaporated. On maceration with 2-propanol, the residual syrup (0.35 g) gave **4** (0.15 g, 50% yield), m.p. and mixed m.p. 141–142°, $[\alpha]_D$ −85.0° (*c* 0.2, $CHCl_3$), coincident in t.l.c. with a pure sample. In this anomerization, part of the acetate is acetolyzed to a mixture of acetylated monosaccharides that remain in solution.

(*b*). Compound **5** (320 mg) was anomerized as described for **2**. The mixture was kept for 9 days at 50°, with stirring. After the usual processing, the residual syrup, dissolved in 2-propanol, gave 156 mg (48.8%) of starting material. In t.l.c., the mother liquors showed **5**, one spot for the β anomer **3** (R_F 0.72), and other spots (R_F up to 0.80) attributable to monosaccharide acetates. No further crystalline substances were obtained.

ACKNOWLEDGMENTS

The authors are indebted to Prof. Jorge O. Deferrari for his interest, to UMYMFOR (CONICET-FCEN, Buenos Aires) and Central Analitica (CPPN-Rio de Janeiro) for instrumental facilities and spectra, and to SECYT for partial, financial support.

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