CONFORMATIONS OF ACYCLIC SUGAR DERIVATIVES

PART II*. DETERMINATION OF THE CONFORMATIONS OF ALDITOL ACETATES IN SOLUTION BY THE USE OF 250-MHz N.M.R. SPECTRA

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ABSTRACT

The p.m.r. spectra of all the fully acetylated pentitols and several fully acetylated hexitols have been analysed. Computation by iterative analysis and recourse to 250-MHz spectra were required in several cases. The vicinal coupling constants were used to determine the conformations of these compounds in solution. The planar zigzag conformation was found to be predominant only in those configurations (*arabino*, *manno*) which do not possess parallel 1,3-interactions between acetoxyl groups on alternate carbon atoms. The other compounds were found to be mixtures of two or more conformers, none of which has the planar zigzag conformation, except in the case of hexa-*O*-acetylallitol. The conformations of alditols in the crystalline state and of the alditol acetates in solution are compared.

INTRODUCTION

There has been considerable interest recently in the conformations taken up by acyclic derivatives of sugars in solution. Numerous derivatives, in which the aldehyde group was replaced by other groups, or substituents were used to prevent ring-closure, have been investigated by the use of p.m.r. spectroscopy[1–11]. Before these investigations, there was a general belief, based only on instinct, that the acyclic derivatives of sugars would be found in a conformation having an extended, planar, zigzag arrangement of carbon atoms, like that of the straight-chain hydrocarbons. A study of the p.m.r. spectra, however, showed that the planar zigzag conformation is predominant only when it does not include parallel, eclipsed 1,3-interactions between oxygen atoms[1–11]. Therefore, derivatives having *arabino*, *lyxo*, *manno*, or *galacto* configurations in a chain of five or six carbon atoms, respectively, are found in the planar zigzag form. Derivatives having other configurations, however, are predominantly

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in conformations derived from the planar zigzag form by a rotation of 120° around one or two carbon–carbon bonds, in order to avoid the 1,3-interaction of oxygen atoms. The term "sickle" has been proposed as a designation of this non-linear or bent conformation[5].

It appeared desirable to test whether these conclusions apply to the simplest, acyclic sugar derivatives, namely to the alditol acetates which contain no groups (other than acetoxy) having large steric or electronic effects. The alditols are also interesting subjects for such an investigation because their conformations in the crystalline state have been investigated in detail. Jeffrey and Kim[12] have concluded that the same considerations which apply to solutions also govern the arrangement of the alditol molecules in crystals, namely, planar zigzag conformations for arabinitol, lyxitol, mannitol, and galactitol, but "bent" forms for the other pentitols and hexitols. In the crystalline state, however, the choice of conformation may also be influenced by the existence of intermolecular hydrogen bonds, and it is not certain that the conformations which exist in the crystal for alditols will also predominate in solution for acetates[13].

Most of the previous work on the conformation of acyclic sugar derivatives was carried out on compounds which contain only three consecutive asymmetric carbon atoms. Of those containing four such carbon atoms, some derivatives having the *manno* and *galacto* configuration have been studied[5,8,9]; these are, however, of comparatively little interest since they are predictably in the planar zigzag conformation, there being no parallel 1,3-interactions in this form. Some derivatives having the *gluco* configuration have also been studied[9]; these were found mainly in one of the "bent" conformations. The most-interesting compounds are those of the *allo* and *ido* configuration but they have not yet been studied. In these compounds, the planar zigzag form has *two* parallel 1,3-interactions; they can be relieved by *one* rotation to the *gauche* form in the center of the molecule, or by two *gauche* arrangements on the two sides of the center. Jeffrey and his co-workers[14] found that, in the crystalline state, D-iditol has the "once-bent", and allitol the "twice-bent", conformation. Hence, it was of considerable interest to study the behaviour in solution of compounds having these configurations.

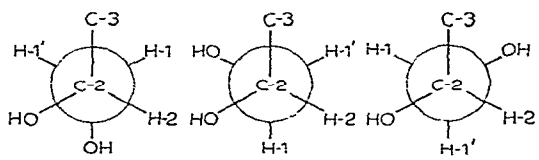
METHODS AND RESULTS

The p.m.r. spectra of the fully acetylated alditols in chloroform-*d* solution were studied. Because each carbon atom has the same group (OAc) attached to it, the signals of the hydrogen atoms are in a narrow range and the spectra are not of first order. The chemical shifts and coupling constants were therefore determined by computation. In several cases, the chemical shifts of H-2, 3, 4, and 5 in the hexitol acetates were not sufficiently different and analysis could be carried out only after 250-MHz spectra became available. Data were obtained by iteration, which ultimately produced computed spectra in satisfactory agreement with those experimentally obtained.

The signals in the p.m.r. spectra occur in three regions. At highest field ($\delta \sim 2.1$) are the signals of the acetyl groups; these provide no information on the conforma-

tions. At mid-field (δ 4.0–4.4) are the signals of the four hydrogen atoms on the terminal carbon atoms, CH_2OAc. For each extremity, these appear as the AB part of an ABX spectrum, that is, two pairs of doublets. Very often, additional lines for H-1 and H-1′, for instance, appear owing to "virtual coupling" with H-3 if $J_{2,3}$ is not sufficiently small; each line is then replaced by a triplet, but the analysis can be performed by using the chemical shift of the central line. In the symmetrical compounds (ribitol, xylitol, allitol, L-iditol, D-mannitol, galactitol), the two end-groups are magnetically equivalent and therefore show identical signals: $\delta_1 = \delta_5$ (or δ_6) and $J_{1,1'} = J_{5,5'}$ (or $J_{6,6'}$), etc. The vicinal and geminal coupling constants of the terminal hydrogen atoms are then obtained by first-order analysis. In the unsymmetrical compounds, the two end-groups are different, and the signals observed are formed by superposition of the AB parts of the two ABX systems. Owing to the regular features of the AB pattern, it is possible to distinguish the lines belonging to each set. The question remains: which set of peaks is due to which end-group? This question was answered by replacing one or both of the hydrogen atoms in one end-group by deuterium atoms (by reducing the corresponding aldose or aldonolactone with sodium borodeuteride). This procedure also allows definite identification of the other protons (distinction between H-2 and H-5, H-3 and H-4).

The terminal methylene groups can also be identified by their coupling constants. The conformation of the terminal hydroxymethyl groups has been discussed by Lee and Scanlon[9], and by Horton and Wander[8]. Of the three possible staggered conformations (*A*, *B*, *C*), the one (*A*) involving the least number of gauche interactions



A *B* *C*

is favoured. If the two carbon atoms adjacent to the terminal group are in the *erythro* configuration, conformation *C* involves parallel 1,3-interactions between the two hydroxyl groups on C-1 and C-3 and is therefore only a minor component in the conformational equilibrium. If C-2 and C-3 are in a *threo* configuration, conformation *B* has such an interaction. The third conformation, *B* and *C*, respectively, is populated to a considerable extent. It can be seen that, in the case of neighbouring *erythro* carbon atoms, H-1 and H-2 form a dihedral angle of 60° in both predominant forms, and hence their coupling constant is ~2.5 Hz. When the neighbouring carbon atoms are in *threo* configuration, the presence of conformation *C*, with a dihedral angle of 180° between H-1 and H-2, increases the average coupling-constant which then has a value of ~5 Hz. Thus, it is found that, at one end of the arabinitol molecule, the vicinal coupling is 2.35 Hz, at the other 4.8 Hz. The other, larger coupling (between H-1′ and H-2) is of no diagnostic value.

The third group of signals in the n.m.r. spectrum, between δ 5.2 and 5.4, represents H-2,3,4 in the pentitols, and H-2,3,4,5 in the hexitols, that is, the hydrogen atoms the couplings of which give information on the conformation of the chain. These signals are not well-separated, and do not lend themselves to first-order analysis. They are particularly complex in the symmetrical molecules, where they represent the ABB′ part of an ABB′XX′YY′ pattern in the pentitols, and the AA′BB′ part of an AA′BB′XX′YY′ pattern in the hexitols. Iterative computation and, in some cases, the use of high-field p.m.r. spectra were required to analyse these spectra.

The spectrum of each alditol acetate is discussed separately in the following section; the chemical shifts and coupling constants are shown in Tables I and II, respectively.

TABLE I

CHEMICAL SHIFTS[a] (δ) OF ALDITOL ACETATES[b] IN CHLOROFORM-*d*

Alditol	*H-1*	*H-1′*[c]	*H-2*	*H-3*	*H-4*	*H-5*	*H-5′*[c]	*H-6*	*H-6′*[c]
D-Arabinitol	4.28	3.94	5.37	5.38	5.14	4.23	4.14		
Ribitol	4.41	4.22	5.28	5.36	5.28	4.41	4.22		
Xylitol	4.44	4.09	5.34	5.45	5.34	4.44	4.09		
Allitol	4.35	4.13	5.24	5.36	5.36	5.24		~4.35	4.23
L-Iditol	4.32	4.06	5.25	5.34	5.34	5.25		4.32	4.06
Galactitol	4.27	3.84	5.29	5.35	5.35	5.29		4.27	3.84
D-Glucitol	4.22	3.89	5.10	5.28	5.26	4.90		4.12	3.98
D-Mannitol	4.08	3.93	4.92	5.30	5.30	4.92		4.08	3.93
Erythritol	4.28	4.14	5.21	5.21	4.28	H-4′ 4.14			

[a]The n.m.r. spectra were measured at 100 MHz with a Varian HA-100 spectrometer with the probe at ~30°, and at 250 MHz with a Thomson-CSF TSN-250 spectrometer with the probe at about 18°, both with tetramethylsilane as the lock signal and internal standard. [b]The acetates were prepared by acetylation of the alditols and had melting points in accordance with published values. [c]When two protons are present on one carbon atom, the one resonating at higher field is designated with a prime.

TABLE II

COUPLING CONSTANTS (IN Hz) OF ALDITOL ACETATES IN CHLOROFORM-*d*[a]

Alditol	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{5,5'}$	$J_{6,6'}$
D-Arabinitol	−11.6	4.8	7.1	2.8	8.5	2.3	5.1			−12.3	
Ribitol	−12.5	3.3	6.4	5.5	5.5	3.3	6.4			−12.5	
Xylitol	−11.9	4.2	6.0	5.2	5.2	4.2	6.0			−11.9	
Allitol	−12.2	2.8	6.1	5.6	4.3	5.6		2.8	6.1		−12.2
L-Iditol	−11.8	4.2	5.7	4.8	5.5	4.8		4.2	5.7		−11.8
Galactitol	−11.5	4.6	7.2	1.8	10.0	1.8		4.6	7.2		−11.5
D-Glucitol	−12.0	4.0	6.1	6.4	4.3	6.8		3.6	5.6		−12.6
D-Mannitol	−12.3	2.6	5.3	9.0	2.2	9.0		2.6	5.3		−12.3
Erythritol	−12.7	2.95	5.7	6.5	2.9	$J_{3,4'}$ 5.7, $J_{4,4'}$ −12.7					

[a]See footnote to Table I.

Tetra-O-*acetylerythritol.* — This molecule, being symmetrical, has equivalent end-groups. The signals of the two methylene groups are well-resolved in the spectrum, and first-order analysis, as the AB part of an ABX system, gives $J_{1,2}$, $J_{1',2}$, and $J_{1,1'}$. The signals of H-2 and H-3 form an irregular multiplet in which ten peaks are discernible. Taking the center of the multiplet as δ_2, the LAOCOON III program was used to calculate the spectrum with $J_{2,3}$ values of 5, 6, 7, 8, 9, and 10 Hz. The observed spectrum appeared to be intermediate between those calculated with the coupling constants 6 and 7 Hz. Recalculation, using the value of 6.5 Hz, provided a good fit with the spectrum.

Penta-O-*acetylribitol.* — This compound gives a spectrum of the ABB'XX'YY' type. The XX'YY' part is clearly resolved at δ 4.2–4.4 (Fig. 1), and all of the coupling constants can be obtained by first-order analysis, except the crucial $J_{2,3} = J_{3,4}$. The low-field part of the spectrum containing the signals of H-2, H-3, and H-4 is very poorly resolved at 100 MHz, and attempts to reproduce it by calculations were not successful. The 250-MHz spectrum, however, completely resolved the signals of these

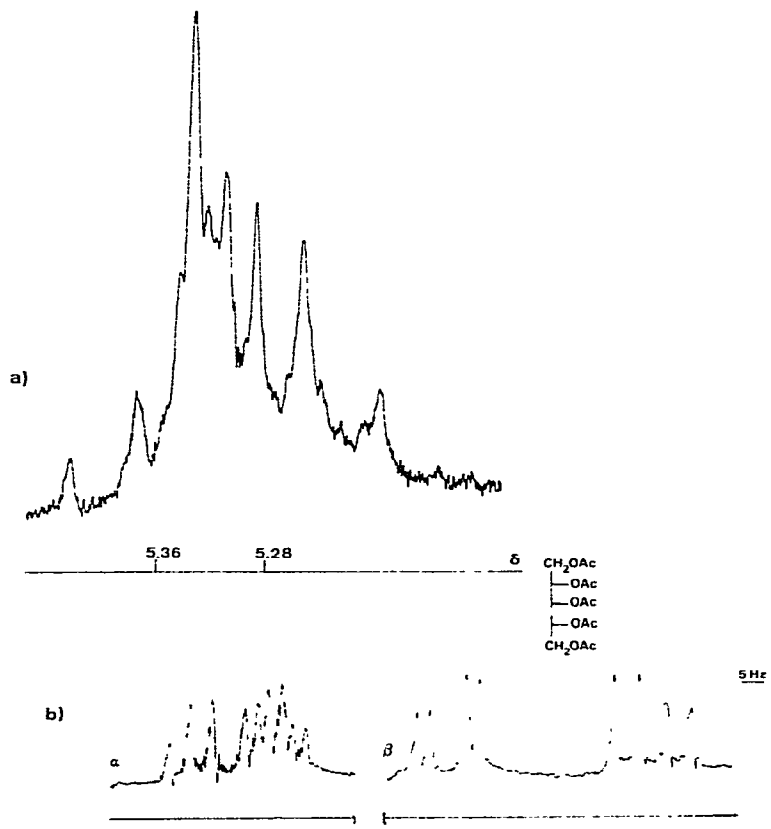


Fig. 1. The low-field portions of the n.m.r. spectra of penta-*O*-acetylribitol in $CDCl_3$: (*a*) at 100 MHz (H-2, H-3, H-4), (*b*) at 250 MHz (α, H-2, H-3, H-4; β = the four methylene protons).

protons, and the chemical shifts and coupling constants could be determined, approximately, by first-order analysis. Two iterations then reproduced the spectrum satisfactorily and gave the data shown in the Tables. Using these data the 100-MHz spectrum was calculated but did not fully coincide with the observed spectrum. This may be due to the different probe temperatures of the two spectrometers; Lee and Scanlon noted[9] the variation of chemical shifts with temperature in acyclic sugar derivatives. The chemical shift of H-3 (δ 5.359 at 250 MHz) was then varied by multiples of 0.002 in the calculations of the 100-MHz spectrum, and almost complete fit was achieved with a value of 5.353.

Penta-O-*acetylxylitol.* — The spectrum of this compound is similar to that of the preceding one and was dealt with in the same way. Calculation, using the provisional parameters obtained from the 250-MHz spectrum, reproduced the 100-MHz spectrum satisfactorily.

Penta-O-*acetyl*-D-*arabinitol.* — The signals near δ 4.0 are those of two non-equivalent methylene groups, and their interpretation in the 100-MHz spectrum was not immediately obvious. However, at 250-MHz, all the peaks are completely separated and first-order analysis is possible. In order to differentiate the two end-groups, a sample of D-arabinose was reduced[15] with sodium borodeuteride; the peaks which remained unaffected by the deuteration are those of H-5 and H-5′. The three-proton multiplet near δ 5.2 allowed an approximate first-order analysis; the parameters thus obtained gave, after iteration by the LAOCOON program, a good fit with the spectum. The resolution of this multiplet was not improved by running the spectrum at 250 MHz. The signals of H-2 and H-4 were differentiated by the observation that only the latter remained unchanged following partial deuteration at C-1.

Hexa-O-*acetyl*-D-*glucitol.* — The spectrum of this compound is complex (Fig. 2), but it was fully analysed, with the aid of partial deuteration, without recourse to 250-MHz spectra. D-Glucono-1,5-lactone was reduced[16], and the product was acetylated to give hexa-*O*-acetyl-D-glucitol-1-d_2. The spectrum now appeared considerably simplified. Of the high-field multiplet, only the peaks darkened in Fig. 2 remained; hence these are the signals of H-6 and H-6′. The multiplet at δ 5.1 collapsed into a rough doublet; this is therefore the signal of H-2, and the separation of the two peaks gave an approximate value (6.4) for $J_{2,3}$. By analogy with the other alditol acetates, the multiplet at δ 5.3 was assigned to H-3 and H-4 and that at δ 4.9 to H-5.

These multiplets were treated as an ABMX system (where H-2 is M, H-5 is X) to obtain δ_{AB}, J_{AB}, J_{AM}, and J_{BX}. It has been shown[17] that, in similar systems, the long-range couplings are small, and they have therefore been neglected. The calculations, however, do not determine which proton is A and which is B. (The reason for this uncertainty is the closely similar magnitude of $J_{2,3}$ and $J_{4,5}$.) Hence, the LAOCOON III program was used to calculate the spectrum, once assuming that $\delta_3 > \delta_4$ and once that $\delta_3 < \delta_4$. The resulting two spectra were closely similar, but the one with H-3 at lower field than H-4 provided a better fit with the experimental spectrum especially for intensities of small, external lines. To refine the parameters, the six-spin, sub-spectrum H-1–H-5 was calculated with the LAOCOON program,

iterating while keeping δ_5 invariant. The shape of the H-3,H-4 multiplet was now exactly reproduced.

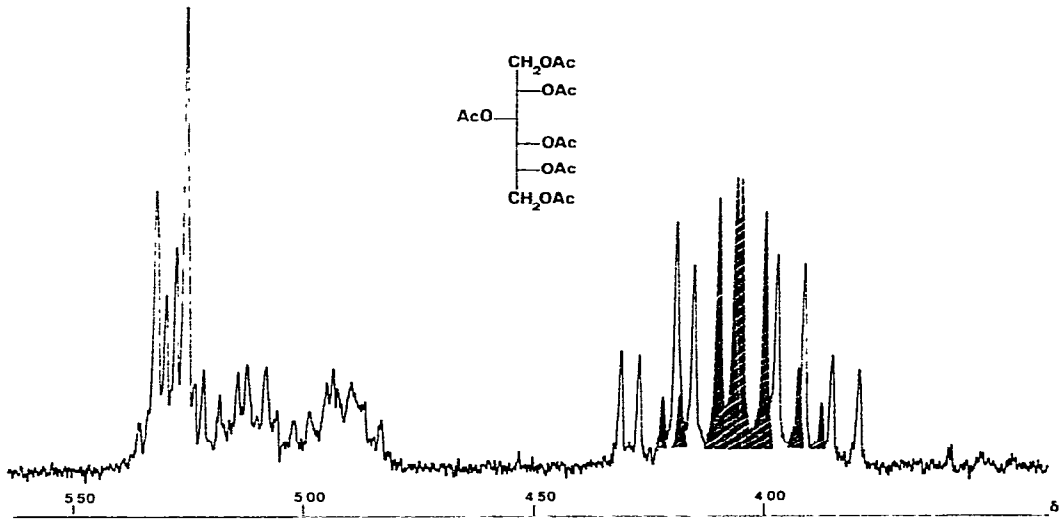


Fig. 2. The low-field portion of the n.m.r. spectrum of hexa-*O*-acetyl-D-glucitol in $CDCl_3$ at 100 MHz (the signals of H-6,6′ are blackened).

Hexa-O-*acetyl*-D-*mannitol.* — The signals of the methylene groups are first order and those of H-2 and H-5 nearly so (Fig. 3). The low-field multiplet of H-3 and H-4, when regarded as the AA′ part of an AA′BB′ spectrum appears to yield the

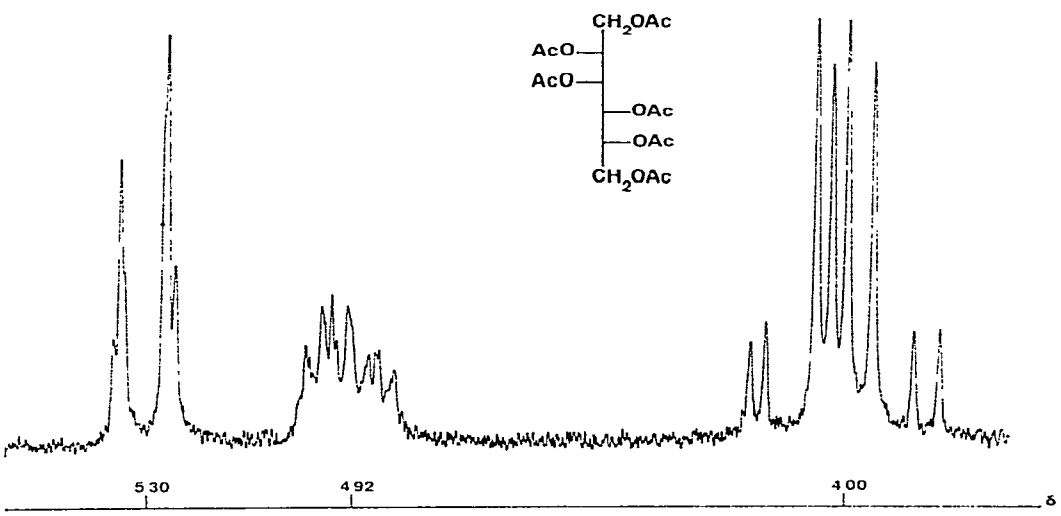


Fig. 3. The low-field portion of the n.m.r. spectrum of hexa-*O*-acetyl-D-mannitol in $CDCl_3$ at 100 MHz.

values $J_{2,3}$ 9 Hz and $J_{3,4}$ 2 Hz. The LAOCOON III program was used to calculate the AA'BB' spectrum and, after one iteration, reproduced the H-3–H-4 multiplet satisfactorily.

Hexa-O-acetylallitol. — This, like the preceding compound, gives a spectrum of the AA'BB'MM'YY' type (where A is H-3, B is H-2, M is H-1, Y is H-1', etc.). If protons A and A' were not present, the signals of B and B' would consist of four transitions, the separation of which can be calculated from the values of $J_{1,2}$ and $J_{1',2}$. The BB' part of the spectrum, at first approximation, would then consist of the superposition of four AA'BB' sub-spectra based on the above separation. Analysis of these subspectra with the LAOCOON III program gave, after iteration, the parameters shown in Tables I and II; using these parameters, the LAME program reproduced both the 60-MHz and the 100-MHz spectra (which differ considerably from each other) very satisfactorily (Fig. 4). Because the values of $J_{2,3}$ and $J_{3,4}$ proved to be somewhat unexpected, they were also determined by studying the couplings of the ^{13}C satellites[18]; this caused only a slight change in the parameters.

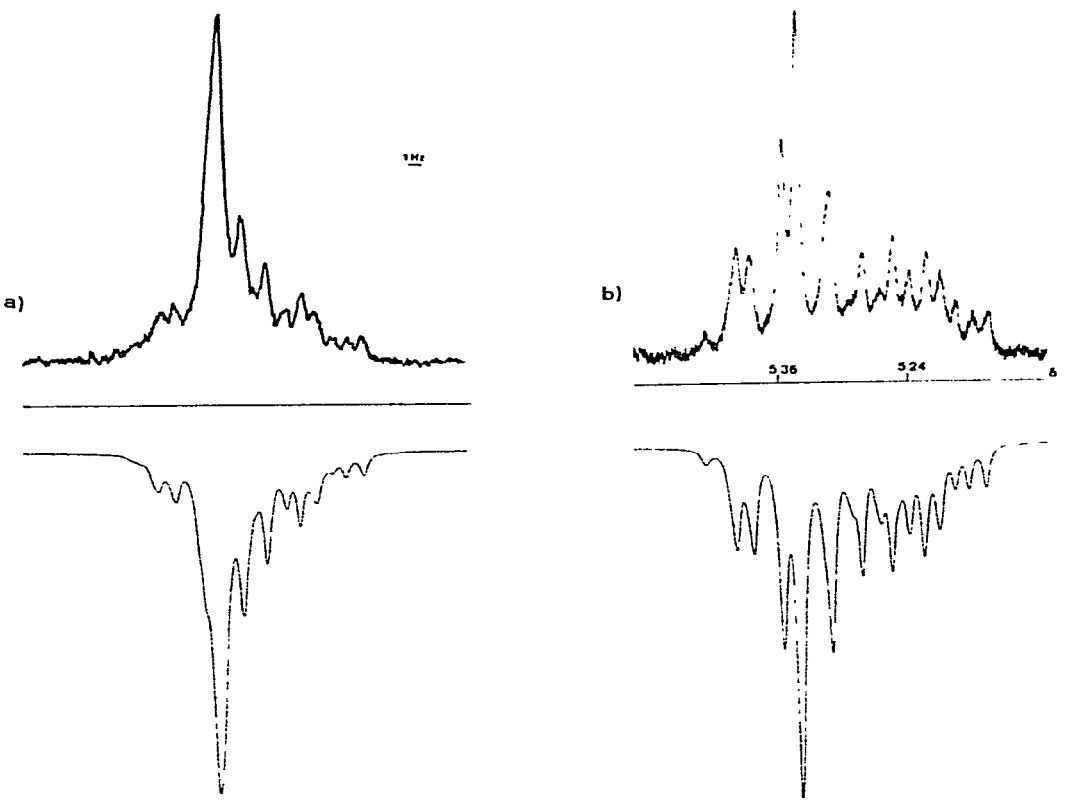


Fig. 4. The H-2–H-5 part of the n.m.r. spectra of hexa-*O*-acetylallitol in $CDCl_3$: (*a*) at 60 MHz, (*b*) at 100 MHz. Upper spectra are experimental spectra, lower spectra are simulated spectra.

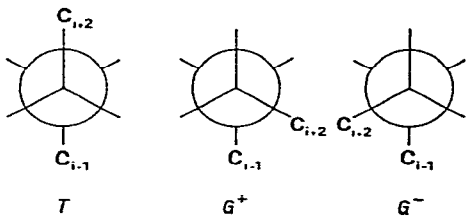
Hexa-O-*acetyl*-L-*iditol.* — The signals of H-2–H-5 are not sufficiently resolved at 100 MHz to provide parameters for calculations. At 250 MHz, however, H-2/5 and H-3/4 are well separated. Iteration at 250-MHz gave a theoretical spectrum with good fit, but the scale of the 250-MHz spectrum does not provide very accurate parameters. Using the parameters obtained at 250-MHz, the 100-MHz spectrum was simulated; iteration gave a good fit but here poor resolution of the spectrum limits the precision of the results. In some cases, the coupling constants calculated for the two spectra differ by as much as 0.5 Hz. The 100-MHz results are regarded as more accurate and are shown in the Tables.

Hexa-O-*acetylgalactitol.* — In this case, the signal of H-3/4 is completely degenerate and does not allow calculation of $J_{3,4}$. This coupling constant was obtained by studying diethylene glycol ^{13}C satellites and acetate as a model, where the two couplings of the ^{13}C with protons have been determined[18].

DISCUSSION

The discussion will be limited to conformational aspects arising from the vicinal J values; the results also add some new data on two points: (*a*) the relationship between the values of geminal coupling constants and the *threo* or *erythro* nature of terminal groups[19], as pointed out to us by Dr. D. J. Stevens; and (*b*) the values of chemical shifts of protons: a proton which has an acetoxyl group antiparallel to it will resonate ~0.2 p.p.m. to lower field than one which has not[1].

For discussion, a simple verbal description of the conformations is required. The term "zigzag form" is unambiguous; however, "sickle" only denotes a departure from the zigzag form, without specifying how many *gauche* arrangements there are and where they are located. We shall follow a notation[20] used in the description of chain polymers, for the arrangement of the sequence C_{i-1}, C_i, C_{i+1}, C_{i+2}, by using T, G_+, and G_- as illustrated below.



Previous experience[1–11] has shown that conformations containing 1,3-parallel interactions are not populated to any significant extent; these will therefore be disregarded. Taking into account all the staggered conformations lacking such interaction, one finds that three hexitols can have only one conformation each, and the

three others can have two each. In the former group, one finds galactitol (*TTT*, **4**)*, allitol (G_+TG_-, **5**), and D-talitol (G_+TT, **6**); in the latter, D-mannitol (*TTT*, **7a** or $G_+G_+G_+$, **7b**), L-iditol (G_-TG_-, **8a** or TG_+T, **8b**), and D-glucitol (G_-TT, **9a** or TG_+G_+, **9b**) (and their enantiomers).

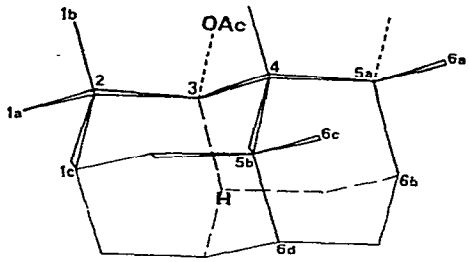


Fig. 5. Congressane skeleton showing the different conformations for hexitol acetates having the (*R*)-configuration at C-3.

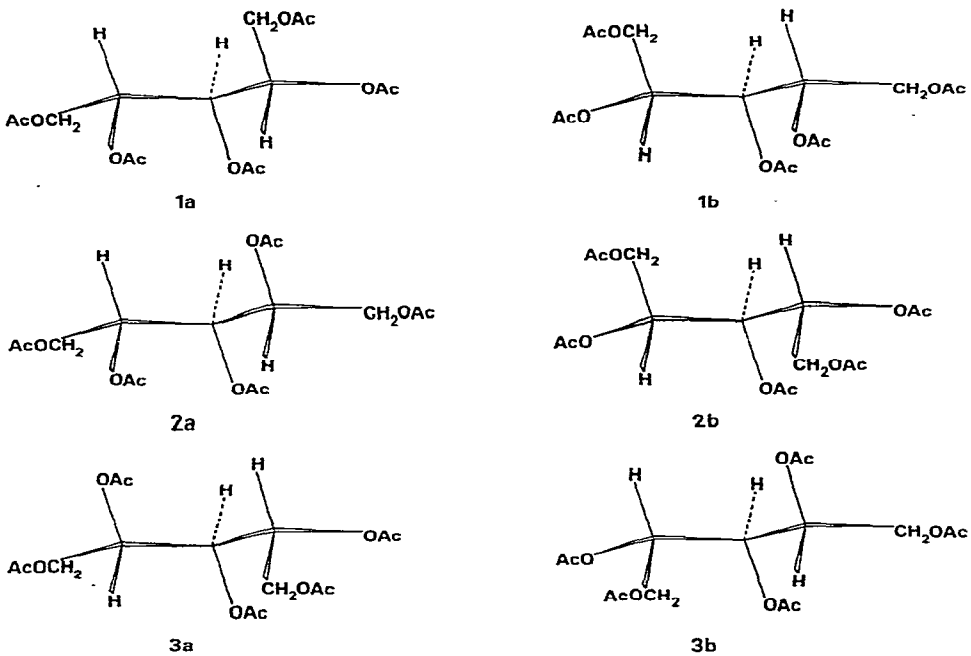
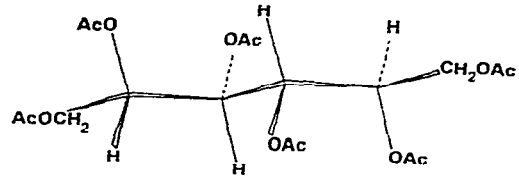


Fig. 6.

*It is difficult to illustrate the possible arrangements of a hexitol satisfactorily; the usual formulae do not show, for example, the 1,3-interactions at a glance. In order to assist the reader, we illustrate these conformations with reference to a readily visualized, steric arrangement, namely that of congressane (Fig. 5). The edges of this structure and some bonds connecting its hydrogen atoms are used for all the conformations of hexitol acetates having the (*R*) configuration at C-3, and the lower front edges of the congressane formula for enantiomeric derivatives; the pentitol acetates **1–3** are illustrated in the latter way, and the hexitol acetates **4–9** in the former way. Formulae **4–9** are particularly easily visualized if the eyes are allowed to accustom themselves for a few seconds to the congressane formula.



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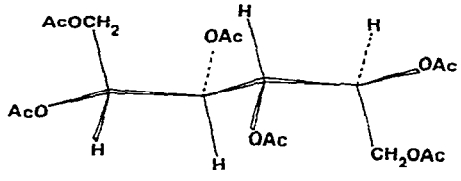

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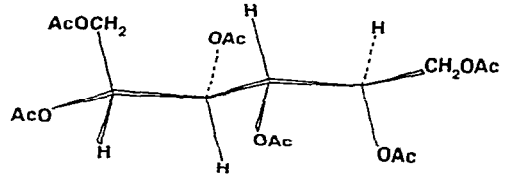

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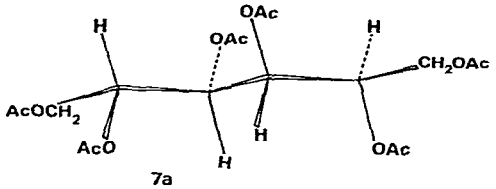

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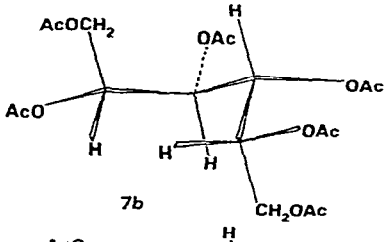
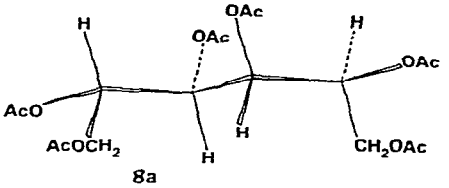
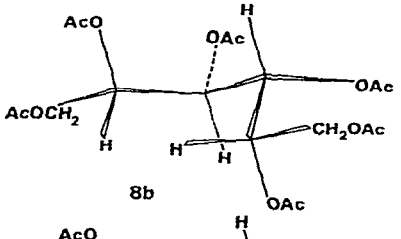


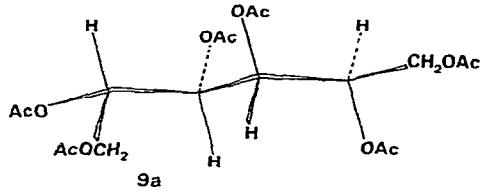
7b



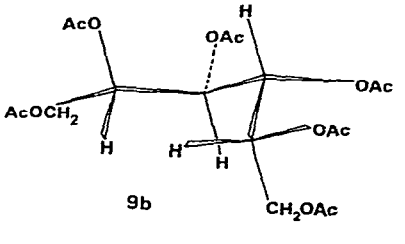
8a



8b



9a



9b

Fig. 6. Theoretical possible conformations without 1–3 parallel interactions: for pentitol acetates (1–3), for hexitol acetates having only one such conformation (4–6), and for hexitol acetates having two such conformations (7–9).

In the planar zigzag conformation of an alditol, the coupling constant betweer two hydrogens on *erythro* carbon atoms is 9.0–9.5 Hz, that between *threo* carbor atoms 2.0–2.5 Hz. A glance at Table II shows that the acetates of D-arabinitol (**2a**) galactitol (**4**), and D-mannitol (**7a**) are in the planar zigzag (*TT* and *TTT*) conformation; the other possible conformation of mannitol ($G_+G_+G_+$, **7b**), having three *gauche* arrangements, must be much less stable.

Ribitol and xylitol both have parallel 1,3-interactions in their planar zigzag forms, and the coupling constants show that another conformation is predominant. Both molecules are symmetrical and therefore rotation by 120° to a "sickle" form will occur equally at the bond between C-2 and C-3 and at the bond between C-3 and C-4. The two "sickle" forms, G_+T and TG_- or TG_+ and G_-T, are enantiomorphs. The observed coupling constants are the averages of those for the two conformations, the calculated value being 5.5 Hz. The "sickle" forms have also been found to be present in the crystal structures of these compounds[12].

In the planar zigzag form of D-glucitol, there is a parallel interaction between O-2 and O-4. This can be eliminated by rotation around the C-2–C-3 or the C-3–C-4 bonds; the latter rotation, however, introduces a new parallel 1,3-interaction between C-2 and O-5, which, in turn, can be eliminated by rotation around the C-4–C-5 bond. The G_-TT form (**9a**) obtained by one rotation is the one found in the crystal structure[12]; the coupling constants, however, show that, in solution, hexa-*O*-acetyl-D-glucitol is a mixture of about two thirds of **9a** and one third of **9b**. (The coupling constants for **9a** would be $J_{2,3}$ 9, $J_{3,4}$ 2, and $J_{4,5}$ 9 Hz; for **9b**, they would be 2, 9, and 2 Hz; and for the planar zigzag, 2, 2, and 9 Hz). This is to be expected since **9a**, with one *gauche* interaction, would be more stable than **9b**, with two.

In the planar zigzag form of L-iditol, there are two parallel 1,3-interactions. They can be removed by two rotations around the C-2–C-3 and C-4–C-5 bonds to give form **8a**, or by one rotation around the C-3–C-4 bond to give form **8b**. The expected coupling constants for **8a** are 9, 2, and 9 Hz, for **8b** 2, 9, and 2 Hz, and for the zigzag form 2, 2, and 2 Hz. The observed coupling constants indicate that, in solution, the hexa-acetate of L-iditol is mainly in conformations **8b** and **8a**, the former (with only one *G* conformation) predominating somewhat. In the crystal, D-iditol occurs[14] in conformation **8b**.

The behaviour of hexa-*O*-acetylallitol is unexpected. In its planar zigzag conformation, it has two parallel 1,3-interactions. There is only one conformation (**5**), derived from the zigzag form by two rotations, which is free from 1,3-interactions, and this is the conformation found for the free alditol in the crystalline state[14]. In this conformation, the coupling constants would be $J_{2,3}$ 2, $J_{3,4}$ 9, and $J_{4,5}$ 2 Hz. The coupling constants found (5.6, 4.3, 5.6 Hz) differ widely from these values. It appears that not more than half of the molecules are in conformation **5**. There are four possible conformations that each have one 1,3-interaction, and they together may make up the rest of the population. Allitol is therefore an exception to the rule that 1,3-interactions are avoided by alditol acetates in solution.

Tetra-*O*-acetylerythritol was studied as a very simple alditol. There are only

three possible staggered conformations of the carbon chain, and the coupling constant ($J_{2,3}$ 6.5 Hz) shows that, in solution, about two thirds of the molecules are in the *T* (zigzag) form and one third in the two *G* forms, as expected.

It appears, therefore, that, in solution, the alditol acetates are predominantly in one conformation, namely in the planar zigzag form, only when this conformation has no parallel 1,3-interactions. Should such interactions occur, a mixture of several conformations is found in solution. X-ray analyses of the alditols show that the conformation in the crystal is the one which is predominant in the solution of the alditol acetate.

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NOTE ADDED IN PROOF

After completion of this work, we determined the coupling-constant values for hexa-*O*-acetyl-talitol (supplied by Professor Horton, whom we thank here). The molecule is unsymmetrical and, at present, we have not reduced talose in order to differentiate the two end-groups. Nevertheless, the coupling constants of these end-groups, compared with those in Tables I and II, enable us to assign the probable solution with $J_{2,3}$ 3.9, $J_{3,4}$ 7.6, and $J_{4,5}$ 3 Hz.

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