*Carbohydrate Research*, 84 (1980) 201–209
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

# THE $^{13}$C-N.M.R. SPECTRA OF ALDITOLS*

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(Received February 26th, 1980; accepted for publication, March 17th, 1980)

ABSTRACT

The $^{13}$C-n.m.r. signals of the pentitols and hexitols in aqueous solution, and of their acetates in chloroform solution, have been assigned by the use of specifically deuterium-substituted compounds. Qualitative correlations have been established between the chemical shifts and the configuration and preponderant conformation of each of the alditols.

## INTRODUCTION

There has been considerable interest lately in the conformations of alditols. Their crystal structures have been determined[2], and the $^{1}$H-n.m.r. spectra of several derivatives (mainly acetates) of alditols and related, acyclic sugar derivatives have been studied[3–5]. These studies have shown that the acyclic polyols and their derivatives assume mainly an extended, planar, zigzag conformation, provided that it has no oxygen atoms with parallel 1,3-interactions. Were such interactions to be present in the zigzag form, one (or several) 120° rotation(s) around carbon–carbon bonds would occur to avoid them, resulting in a "bent" or "sickle" conformation[3].

The free alditols in aqueous solution are of particular interest, but their n.m.r. spectra are uninformative, as most of the proton signals coincide. By augmenting the spectral dispersion by incremental additions of europium salts, Angyal *et al.*[1] concluded that the pentitols and hexitols take up the same conformations in aqueous solution as do their acetates in organic solvents.

The conformations of heptitols and higher alditols have not yet been studied, but they would be expected to show some interesting features[6]. In particular, among them, diastereomers exist that can have no conformation free from 1,3-parallel interactions. Because their study by $^{1}$H-n.m.r. spectroscopy appeared unpromising, we decided to explore $^{13}$C-n.m.r. spectroscopy as a method for determining their conformations.

*Conformations of Acyclic Sugar Derivatives, Part V. For Part IV, see ref. 1.

The $^{13}$C-n.m.r. spectra of several alditols have already been reported. Voelter *et al.*[7] determined the spectra of the pentitols and of three hexitols. The $^{13}$C signals were tentatively assigned by comparisons of the spectrum of each alditol with those of others; this procedure gave the right assignments for the symmetrical compounds, but the wrong one for glucitol. In a later paper, Voelter *et al.*[8] changed the (correct) assignments for galactitol, arguing from the results of comparison of its spectrum with those of two partially methylated galactitols. In this case, the procedure is ambiguous and could have given the right answer just as easily as the wrong one. The wrong assignment for the signals of glucitol was also derived by Colson *et al.*[9].

While our work was in progress, Kieboom and his co-workers[10] assigned the signals in the $^{13}$C-n.m.r. spectrum of D-glucitol by an unambiguous method, that is, by the study of D-[1-$^{2}$H]glucitol and D-[5-$^{2}$H]glucitol. We derived the same assignments by using D-[2-$^{2}$H]glucitol and D-[5-$^{2}$H]glucitol. The result was not readily predictable by using analogies with other compounds.

The other three hexitols had not yet been studied. We therefore set ourselves the aims of (*i*) assigning the $^{13}$C-n.m.r. signals in the spectra of all of the hexitols in deuterium oxide solution; (*ii*) establishing correlations between the chemical shifts in the spectra and the configuration and conformation of each of the hexitols; and (*iii*) thereby finding means for studying the conformations of the higher alditols by the use of $^{13}$C-n.m.r. spectra. These objectives have been achieved.

After our work had been completed, a paper was published by Szarek and his co-workers[11] in which the $^{13}$C spectra of the pentitols and the hexitols in deuterated $Me_2SO$ were fully assigned. Despite the different solvent, most of our data agree well with theirs, but there are some divergences to which attention will be called. For their assignments, they used comparisons of the alditols with each other and with other related compounds, a method not without ambiguities. Thus, our data show that their argument for the assignment of the peaks in the spectra of allitol and altritol is not necessarily correct, and we consider that their assignment for C-2 and C-3 of allitol should probably be reversed.

## RESULTS

In the $^{13}$C-n.m.r. spectrum of every alditol in deuterium oxide, all signals were separated from each other. (In deuterated $Me_2SO$, some signals of ribitol and altritol overlap[11].) Those of the terminal carbon atoms appear at higher field (~64 p.p.m.) than the others. Assignment of the remaining signals is obvious only for the tetritols, and for ribitol and xylitol. To assign the other signals in an unequivocal way, extensive use was made of specifically deuterated alditols. We observed not only the disappearance of the signal of the carbon atom to which the deuterium atom had been attached[12], but also the upfield shift of the signals of the neighboring carbon atoms, the *β-shift*[13]. The *β*-shift has been extensively used by Gorin[14] to assign the signals in the $^{13}$C spectra of sugars and glycosides; in these cases, the *β*-shift is smaller (0.04–0.10 p.p.m.) than in the spectra of hydrocarbons, and is often not clearly

observed when two spectra are compared. It is readily seen, however, when samples of the deuterated and the undeuterated compounds are mixed and the spectrum is recorded: the signals subject to $\beta$-shift appear as doublets, or at least as broad singlets, whereas the other signals are sharp singlets.

The signals in the spectrum of arabinitol, for example, were assigned as follows. D-Arabinose was reduced with sodium borodeuteride, and the spectrum of the resulting D-[1-$^2$H]arabinitol was compared with that of D-arabinitol. The line at $\delta$ 64.4 had disappeared (C-1) and that at $\delta$ 71.9 had shifted upfield by 0.05 p.p.m. (C-2). Similar reduction of D-lyxose allowed the assignment of the signal at $\delta$ 64.3 to C-5 (disappearance), and that at $\delta$ 72.3 to C-4 (upfield shift of 0.07 p.p.m.), of arabinitol.

A more efficient procedure was used to assign the signals of the hexitols. 2-Hexuloses were reduced by sodium borodeuteride, thereby introducing deuterium onto C-2; the $\beta$-shift then also identifies C-1 and C-3. Two hexitols are formed in each reduction, but it was found unnecessary to separate them: all of the signals could be identified in the spectrum of the mixture by reference to the spectra of the pure components. In this way, one reaction allows the assignment of six $^{13}$C signals, three for each hexitol. By the reduction of D-fructose, L-sorbose, D-psicose, and D-tagatose, all of the $^{13}$C signals of the hexitols could thus be assigned.

As a cross-check, and because the assignment of C-3 in D-altritol appeared to be not fully convincing, we prepared a mixture of D-[3-$^2$H]mannitol and D-[3-$^2$H]-altritol by the reduction of D-*arabino*-3-hexulose[15]. The spectra gave a clear definition of C-3 of the latter hexitol, and confirmed the assignments for the former. As an illustration of the method, details of the spectra of this mixture are given in Table I: the signal of C-3 of each compound disappears on deuteration, and those of C-2 and C-4 shift upfield by 0.04–0.05 p.p.m. The two-carbon mannitol signal at $\delta$ 70.66 is decreased by half, and shifted upfield, confirming that it is the signal of C-3 and C-4. The signals of C-1 and C-5 of altritol showed the $\gamma$-effect also; this effect, which is usually very small[13] (0.01–0.02 p.p.m.), was observed in a few other instances, but it is of no diagnostic value.

The assignments made for the alditols by these approaches are listed in Table II. All of the signals of each alditol are separated from each other, whereas, in deuterated

TABLE I

ASSIGNMENT OF THE $^{13}$C CHEMICAL-SHIFTS OF THE REDUCTION PRODUCTS OF D-*arabino*-3-HEXULOSE

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\delta$ (p.p.m.), *non-deut*[a] | 63.38 | 64.37 | 64.58[b] | 70.66[b] | 71.83 | 72.15 | 72.24[b] | 72.95 | 73.95 |
| $\delta$ (p.p.m.), *deut*[c] | 63.38 | 64.36 | 64.58[b] | 70.60 | 71.78 | | 72.20<br>72.24 | 72.91 | 73.93 |
| *Hexitol*[d] | A | A | M | M | A | A | M | A | A |
| *Assignment* | C-6 | C-1 | C-1,6 | C-3,4 | C-2 | C-3 | C-2,5 | C-4 | C-5 |

[a]Mixture obtained by reducing D-*arabino*-3-hexulose with $NaBH_4$. [b]Two-carbon signal. [c]Mixture obtained by reducing D-*arabino*-3-hexulose with $NaBD_4$. [d]A = altritol, M = mannitol; by comparison with spectra of the pure hexitols.

TABLE II

$^{13}C$ CHEMICAL-SHIFT DATA[a] OF THE ALDITOLS

| *Compound* | *C-1* | *C-2* | *C-3* | *C-4* | *C-5* | *C-6* |
|---|---|---|---|---|---|---|
| Ethylene glycol | 63.8 | 63.8 | | | | |
| Glycerol | 64.0 | 73.5 | 64.0 | | | |
| Erythritol | 64.0 | 73.3 | 73.3 | 64.0 | | |
| Threitol | 63.9 | 72.9 | 72.9 | 63.9 | | |
| Arabinitol | 64.4 | 71.6 | 71.9 | 72.3 | 64.3 | |
| Ribitol | 63.8 | 73.5 | 73.6 | 73.5 | 63.8 | |
| Xylitol | 63.9 | 73.2 | 72.0 | 73.2 | 63.9 | |
| Allitol | 63.7 | 73.5 | 73.7 | 73.7 | 73.5 | 63.7 |
| Altritol | 64.4 | 71.8 | 72.2 | 73.0 | 74.0 | 63.4 |
| Galactitol | 64.5 | 71.5 | 70.7 | 70.7 | 71.5 | 64.5 |
| Glucitol | 63.8 | 74.3 | 71.0 | 72.6 | 72.5 | 64.2 |
| Iditol | 64.1 | 73.1 | 72.5 | 72.5 | 73.1 | 64.1 |
| Mannitol | 64.6 | 72.2 | 70.7 | 70.7 | 72.2 | 64.6 |

[a]In p.p.m. downfield from external $Me_4Si$ in deuterium oxide.

TABLE III

$^{13}C$ CHEMICAL-SHIFT DATA[a] FOR THE ALDITOL ACETATES

| *Acetate of* | *C-1* | *C-2* | *C-3* | *C-4* | *C-5* | *C-6* |
|---|---|---|---|---|---|---|
| Ethylene glycol | 62.4 | 62.4 | | | | |
| Glycerol | 62.4 | 69.4 | 62.4 | | | |
| Erythritol | 61.9 | 69.4 | 69.4 | 61.9 | | |
| Threitol | 62.0 | 69.4 | 69.4 | 62.0 | | |
| Arabinitol | 62.1 | 68.3 | 68.6 | 68.3 | 61.9 | |
| Ribitol | 61.8 | 69.6 | 69.4 | 69.6 | 61.8 | |
| Xylitol | 62.0 | 69.4 | 69.3 | 69.4 | 62.0 | |
| Allitol | 61.8 | 69.7 | 69.4 | 69.4 | 69.7 | 61.8 |
| Altritol | 62.1 | 68.4 | 69.1 | 68.7 | 70.0 | 61.7 |
| Galactitol | 62.3 | 67.8 | 67.7 | 67.7 | 67.8 | 62.3 |
| Glucitol | 62.0 | 69.6 | 68.7 | 69.0 | 68.9 | 61.6 |
| Iditol | 61.8 | 69.3 | 68.9 | 68.9 | 69.3 | 61.8 |
| Mannitol | 62.0 | 68.1 | 67.7 | 67.7 | 68.1 | 62.0 |

[a]In p.p.m. downfield from internal $Me_4Si$ in deuteriochloroform.

$Me_2SO$, there is some overlap, *e.g.*, of those for C-2 and C-3 of ribitol. (When comparing our data with those of Szarek and co-workers[11], it should be noted that they used $Me_4Si$ as an internal, and we used it as an external, standard. The two scales differ by $\sim$1 p.p.m.) In a few cases, there is a substantial divergence between the spectra in deuterium oxide and in dimethyl sulfoxide: the signals of C-1 and C-6 of altritol overlap in the latter solvent, whereas they are 1.0 p.p.m. apart in $D_2O$. On the other hand, those of C-1 and C-5 of arabinitol almost overlap in $D_2O$, but are widely separated in $Me_2SO$. It would not, therefore, always be justified to interpret

the spectrum of a compound in the one solvent on the basis of assignments made for a solution in the other one.

All of the samples were also acetylated, and the signals of the acetates were assigned in the same way. The following steps were therefore carried out with each ketose: (*i*) reduction by sodium borohydride; (*ii*) reduction by sodium borodeuteride; (*iii*) acetylation of the first reduction-product; (*iv*) acetylation of the second reduction-product; (*v*) mixing of the two products; and (*vi*) deacetylation of the mixture. After each step, the $^{13}$C-n.m.r. spectrum was recorded. The assignments obtained for the alditol acetates are shown in Table III.

## DISCUSSION

Various methods have been developed for establishing quantitative correlations between $^{13}$C chemical-shifts and the spatial relationships between the carbon atoms and other atoms in the molecule[16,17]. Shielding parameters have been assigned to various steric features, and these parameters have been assumed to be additive. When applied to cyclitols and pyranoid sugars, these methods have been moderately successful[18], although it has been shown[19] that, at times, they have led to wrong assignments. We have attempted to rationalize the $^{13}$C chemical-shifts of the alditols by similar methods, but without success. Possible reasons for this failure are (*i*) the greater flexibility of the carbon chains, compared to rings: variations from the idealized, 60° staggering are to be expected[20,21], and these may substantially alter the chemical shifts; (*ii*) the incidence of conformational equilibria in which there is time-averaging of chemical shifts from two or more conformers, of which only the preponderant one is taken into account; and (*iii*) imperfections in the methods tentatively applied.

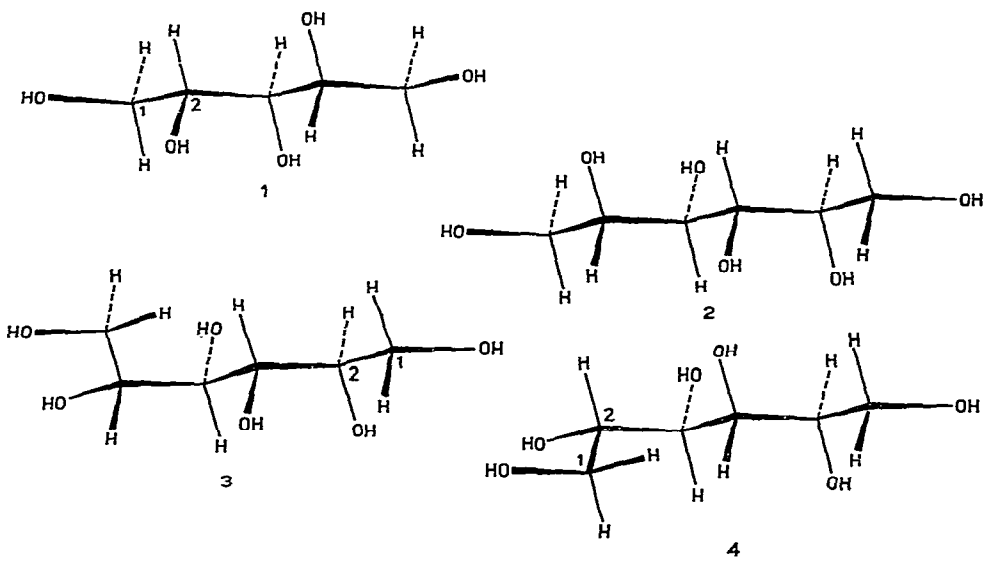
We therefore abandoned the quantitative methods, and found that the variations in chemical shifts could be qualitatively accounted for by considering only two types of interaction: *gauche* interactions between substituents on the carbon atom under consideration and on the neighboring carbon atom, and 1,3-parallel interactions between a hydrogen atom on the carbon atom studied and a substituent on the $\gamma$-carbon atom. It is not claimed that these interactions necessarily are the causes of the variations in chemical shifts; however, they provide practical, empirical rules for understanding the $^{13}$C shifts.

Let us first consider those alditols that are mainly in the extended, planar, zigzag conformation, without 1,3-parallel interactions, namely, arabinitol, mannitol, and galactitol. In the spectrum of D-arabinitol (**1**), C-2 is found at higher field than C-4, by 0.7 p.p.m. The former has an O/O interaction, but the latter does not: such *gauche* interaction therefore shields by 0.7 p.p.m. Similarly, C-2 in galactitol (**2**) resonates 0.7 p.p.m. higher than C-2 in mannitol, for the same reason. If this value is added to the chemical shifts of those carbon atoms which have O/O interactions, then the "normal" chemical shift of C-2 and C-5 in hexitols is 72.2, and of C-3 and C-4, 71.4 p.p.m. Each of the secondary carbon atoms in these zigzag forms is affected by one C/O (*gauche*) and one H//O (1,3-parallel) interaction; the effect of these

interactions is included in the "normal" chemical shifts. The C-3 atom of arabinitol lacks an H//O interaction, and it resonates 1.2 p.p.m. to lower field than C-3 in mannitol or galactitol. The H//O interaction therefore shields by ~1.2 p.p.m. Szarek and co-workers have already pointed out[11] that these shielding parameters (0.7 and 1.2) are much smaller than those found in the rigid cyclohexane or pyranose rings, presumably owing to the flexible nature of the alditol molecules. The chemical shifts of the primary carbon atoms are only slightly affected by the chain-length: 64.0 in tetritols, 64.3–64.4 in arabinitol, and 64.5–64.6 in the two hexitols that are in the zigzag form.

By contrast, the spectra of the alditols that are predominantly in a sickle conformation differ in two respects: one or both of the signals of the terminal carbon atoms are at higher field, and those of some of the secondary carbon atoms at lower field, than the "normal" values. A good example to discuss is D-altritol. There can be little doubt that it would take up the only possible conformation free from 1,3-parallel interactions, the ${}_4G^+$ form (**3**) (that is, the sickle derived from the zigzag form by a 120°, counterclockwise rotation of the remote atom around the C-4–C-5 bond; for definition of this terminology, see ref. 20). Hexa-*O*-acetyl-D-altritol is found to assume this conformation[5]. In this form of altritol, C-1 and C-2 are in the same environment as in galactitol, and have similar chemical-shifts. The signals of C-4 and C-5 are, however, at lower field than the "normal" values, presumably owing to the C/C (*gauche*) interaction; the C/C interaction has been postulated[22] to deshield by 1.2–1.7 p.p.m. The signal of C-3 also appears at lower field; the explanation is probably the presence of an H//C (with the primary C-1), instead of the usual H//O, interaction on H-3. The former is less shielding than the latter[23].

The most stable conformation of D-glucitol is[1,5] ${}_2G^+$ (**4**). In this case, C-6 and C-5 have "normal" chemical shifts, and C-2 and C-4 appear at lower field. The signal



of C-3 is only slightly displaced to lower field, although C-3 is at one end of the *gauche* bond, but the reason for this behavior is not clear. It has an additional O/O interaction, but that is insufficient to explain its high-field location. In deuterated $Me_2SO$, the signals of C-3 of xylitol and glucitol are[11] at even higher field than in deuterium oxide. Conformational mixtures whose composition varies with the solvent are probably being dealt with here.

The signal of C-1 in D-glucitol is at higher field than the "normal" value; one of the hydrogen atoms on C-1 has a 1,3-parallel interaction with C-4 (a secondary carbon atom), instead of the usual H//O interaction. The signal of C-6 in D-altritol is still farther upfield; in this case, one of the hydrogen atoms has a H//C, and the other an H//O, interaction.

$^{13}$C-N.m.r. spectroscopy therefore provides two criteria for the recognition of sickle conformations. When an *erythro-erythro* sequence in an alditol is changed by rotation to a sickle form, the signals of the three carbon atoms in the sequence move downfield by ~2 p.p.m.; when a *threo-threo* sequence is similarly treated, the signals of the two outer carbon atoms move downfield. The signal of the terminal carbon atom moves upfield by ~0.7 p.p.m. on rotating an adjacent bond between carbon atoms bearing *threo* hydroxyl groups; if the relationship is *erythro*, the shift is ~1 p.p.m.

The only conformation of allitol free from 1,3-parallel interactions is $_2G^+{}_4G^-$ ($= {}_2G^-{}_4G^+$); this is the conformation found in the crystal form[24]. The $^{13}$C-n.m.r. spectrum is in accordance with this form's being the preponderant one in solution: the signal of C-1,6 is at higher field, and the other signals at lower field, than "normal"; in particular, C-3,4 are at lower field than the C-3 or C-4 signal of any other hexitol, suggesting a double sickle form. The hexaacetate contains substantial proportions of other forms at equilibrium[4]; however, the steric interaction between 1,3-parallel acetoxyl groups is much smaller than that between similar hydroxyl groups[25].

D-Iditol can avoid 1,3-parallel interactions by taking up the $_3G^-$ conformation; this is the form observed in the crystals[24]. For this form, the chemical shift of C-1,6 should be "normal"; the fact that it is at somewhat higher field shows that other conformations (probably $_2G^+{}_4G^-$) occur in solution to a significant extent. The hexaacetate of D-iditol was found to exist as a mixture of these two conformations[4].

The $^{13}$C-n.m.r. spectra of the alditol acetates (see Table III) are less informative than those of the free alditols. Acetylation causes the signals to shift upfield: those of the terminal carbon atoms by 1.8–2.6 p.p.m., and those of the others by 2.3–4.7 p.p.m. The signals are closer to each other than in the spectra of the alditols, and they could not be assigned with confidence simply by comparing their positions with those in the spectra of the alditols. On acetylation, most of the derivable information as to configurations and conformations is lost, and there is now no distinction between the vicinal *erythro* and *threo* substituents: C-2 has the same chemical-shift for the peracetates of erythritol and threitol, and C-2 has the same chemical shift as C-4 in the peracetate of arabinitol. The chemical shifts of the terminal carbon atoms no longer provide an indication for the presence of a sickle arrangement. It is still possible, however, to detect a sickle conformation at a glance: only the pentitol and

hexitol acetates in a sickle form have, in their spectra, signals with chemical shifts greater than 69.0 p.p.m.

## EXPERIMENTAL

*General.* — Allitol, D-altritol, and D-iditol were obtained from the late Dr. J. A. Mills. D-Psicose was prepared from D-fructose according to Cree and Perlin[26]. The other alditols and ketoses were commercial samples: commercial D-tagatose was purified as described before[19]. The ketoses were reduced[27] with sodium boro-hydride or -deuteride at 4°; some of the ketoses required several days, but D-sorbose gave satisfactory results after standing for one night. Acetylations were conducted[28] with acetic anhydride and pyridine, followed by partition between chloroform and water. Deacetylations were performed catalytically with sodium methoxide in methanol[29].

*N.m.r. spectra.* — The $^{13}$C-n.m.r. spectra were first recorded with a Bruker WP-60 Fourier-transform spectrometer: those of the alditols in deuterium oxide, with tetramethylsilane as the external standard, and those of the acetates in deuteriochloroform, with tetramethylsilane as the internal standard. The signals of arabinitol and of the acetates of xylitol and glucitol were not fully separated; their spectra were then recorded with a Varian XL-100 instrument. Spectra for the detection of the $\beta$-shift were recorded with the Varian spectrometer; in rare instances, they were re-recorded with a Cameca 250 instrument.

## ACKNOWLEDGMENTS

The authors are grateful to the late Dr. J. A. Mills for a gift of samples, to Mr. L. Patron for recording the 60-MHz spectra, to Mr. R. Nardin for obtaining the $\beta$-effects in the 100-MHz spectra, and to Professor D. Gagnaire for providing one of us (R.L.F.) with facilities for this research.

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