

Conformations of some phenylhydrazones of saccharides

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The spatial arrangement of phenylhydrazone of D-erythrose and of the acetylated phenylhydrazone derivatives of D-arabinose, D-galactose, D-fructose, and D-erythrose was concluded from their p.m.r. spectra.

На основании спектров ПМР обсуждено пространственное расположение фенилгидразона D-эритрозы и ацелированных производных фенилгидразонов D-арабинозы, D-галактозы, D-фруктозы и D-эритрозы.

Most of the studies on conformations of acyclic saccharides have been carried out by *Horton* and co-workers [1]. It was assumed that acyclic derivatives of saccharides exist in planar zig-zag arrangement which ensures maximum distance of large substituents on the carbon chain. Such arrangement was proved by p.m.r. spectroscopy in the case of saccharide derivatives of quinoxalines [2]. If in the planar arrangement the oxygen atoms would get into the energetically nonadvantageous 1,3-interaction, the substituents would rotate about the C—C bond forming the "sickle" conformation [3, 4]. The acyclic structure of the saccharide derivatives of phenylhydrazones was proved by p.m.r. spectroscopy in [5].

In our work we discuss the spatial arrangement of the carbon chains of some chosen compounds on the basis of their p.m.r. spectra. The choice of suitable acyclic saccharide derivatives for p.m.r. studies is difficult because most of these compounds show overlapped signals forming multiplets of second order.

Experimental

The studied compounds were prepared according to [6—9] and their physicochemical constants were the same as those found in the literature.

The p.m.r. spectra of the compounds I—IV in CDCl_3 and of the compound V in $\text{DMSO-d}_6 + \text{CDCl}_3$ were measured on a Tesla BS 487 B (80 MHz) at 25°C. Chemical shifts and coupling constants were obtained by direct reading from the first-order part of the

spectra. The coupling constants are given with the accuracy of ± 0.1 Hz. The method of double resonance (INDOR) was used to assign the signals to individual protons.

Results and discussion

As typical representatives of nonrigid saccharides appearing in solutions in acyclic forms we chose 2,3,4,5-tetra-*O*-acetyl-D-arabinose 2,4-dinitrophenylhydrazone (*I*), 2,3,4,5,6-penta-*O*-acetyl-D-galactose 4-nitrophenylhydrazone (*II*), 1,3,4,5,6-penta-*O*-acetyl-D-fructose 2,4-dinitrophenylhydrazone (*III*), 2,3,4-tri-*O*-acetyl-D-erythrose 4-nitrophenylhydrazone (*IV*), and D-erythrose 4-nitrophenylhydrazone (*V*). We considered the mentioned compounds to be in the favoured planar zig-zag and sickle conformations, respectively, with 1,3-interaction as the main destabilizing factor [10].

The signal H-1 with the compounds *I*, *II*, *IV*, and *V* appeared as a doublet between 7.16—7.43 p.p.m. while with *III* as a singlet at 4.88 p.p.m. The H-2 signals with the measured compounds were split into quartet except with *I* which showed a triplet.

The acetylated phenylhydrazones *I*—*IV* had the H-2 signals at 5.79—5.50 p.p.m. and the compound *V* at 4.19 p.p.m. The signals of the proton bound to the nitrogen atom in the derivatives of 2,4-dinitrophenylhydrazone appeared at 11.13—11.85 p.p.m. while in the derivatives of 4-nitrophenylhydrazone at 8.63—10.80 p.p.m. Signals of geminal protons at the end of the carbon chain were found at 4.43—3.94 p.p.m. The signals of aromatic protons appeared at 9.11—6.50 p.p.m. The methyl groups showed sharp singlets at 2.23—2.01 p.p.m.

Table 1

Coupling constants (Hz) of the studied compounds

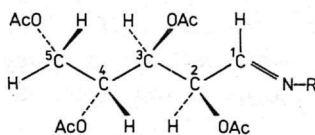
Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
			$J_{3,4'}$	$J_{4,5'}$	$J_{5,6'}$
<i>I</i>	4.2	3.5	7.7	2.9	—
			—	4.8	—
<i>II</i>	5.0	9.0	<i>a</i>	<i>a</i>	7.6
			—	—	4.4
<i>III</i>	—	—	4.0	6.8	2.6
			—	—	5.7
<i>IV</i>	5.0	5.2	2.9	—	—
			6.7	—	—
<i>V</i>	5.0	5.0	<i>a</i>	—	—
			<i>a</i>	—	—

a) Impossible to read off from the spectrum.

In the p.m.r. spectra of acyclic saccharides [11] signals with the following coupling constants appeared most frequently: $\sim 8\text{--}9$ Hz characteristic of vicinal protons with antiparallel arrangement and $\sim 2\text{--}3$ Hz indicating that the vicinal protons are in "gauche" position. Deviations from the mentioned values of the coupling constants indicate a partial disarrangement of the planar zig-zag conformation of the carbon chain by rotation of substituents about the C—C bonds.

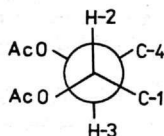
The coupling constants of the compounds I—V are summarized in Table 1.

The coupling constants of the D-arabinose derivative (I) indicated that the hydrogen atoms on C-2 and C-3 were in "gauche" arrangement while on C-3 and C-4 were antiparallel. On the basis of the above-mentioned facts and considering the coupling constants $J_{4,5}$ and $J_{4,5'}$ it can be assumed that at 25°C the chain of the molecule was in the planar zig-zag conformation (Scheme 1)



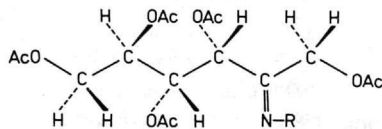
Scheme 1

The high value of $J_{2,3}$ (9 Hz) with the D-galactose derivative II indicated the "sickle" conformation where the H-2 and H-3 were antiparallel. Scheme 2 shows the position of H atoms and substituents on C-2 and C-3 in the compound II.



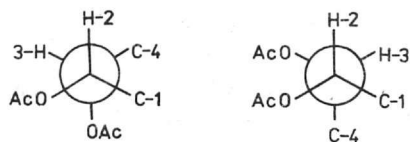
Scheme 2

Considering the coupling constants, the peracetylated hydrazone of fructose III can appear in the favoured planar zig-zag arrangement under the conditions of measurement (Scheme 3). The molecule of the acetylated phenylhydrazone of



Scheme 3

D-erythrose *IV* is not in the planar zig-zag conformation. In this form the H-2 and H-3 would be antiparallel but the value of $J_{2,3}$ indicated a rotation of the substituents about the C-2 and C-3 bonds. Therefore, we assumed that this molecule is in the "sickle" conformation. Scheme 4 shows two alternative equal



Scheme 4

arrangements of the substituents on the C-2 and C-3. The same arrangement could be assigned to the nonacetylated compound *V*.

It is evident from the coupling constants of *V* and of its acetylated derivative *IV* that the acetyl groups had no effect on the spatial arrangement of the molecule of these compounds. This knowledge could not be supported by other facts because most of the mentioned compounds had the spectra of second order showing overlapped signals which could not be analyzed even by using a shift reagent (europium nitrate).

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