## Note

# Conformations of acyclic sugar derivatives Part III[1]. 3,4,5,6,7-Penta-acetoxy-*trans*-1-nitro-1-heptenes

S. J. ANGYAL,

*School of Chemistry, The University of New South Wales, Kensington, N. S. W. 2033 (Australia)*

R. LE FUR, AND D. GAGNAIRE*

*Laboratoire de Chimie Organique Physique du Centre d'Études Nucléaires de Grenoble, Cedex 85, 38 Grenoble-Gare (France)*

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In 1969, Williams[2] published an analysis of the p.m.r. spectra of the tetra-acetoxy-*trans*-1-nitro-1-hexenes having the D-*arabino*, D-*xylo*, and D-*ribo* configurations and concluded that, in solution, only the *arabino* isomer has the planar zigzag conformation of the carbon skeleton (C-2–C-6). The other two isomers would have unfavourable non-bonded interactions between acetoxyl groups on C-3 and C-5 in the zigzag conformation; this interaction is avoided by a 120° rotation around one of the carbon–carbon bonds.

Owing to current interest in the conformations of acyclic derivatives of sugars[1,3], we were working on unsaturated nitro derivatives of alditols at the time Williams's paper appeared. Our results for the three hexene derivatives agree well with his and are therefore not described. However, we have also included in our study several seven-carbon analogues which allow greater scope for conformational variations. The D-*manno* isomer gave unsatisfactory p.m.r. spectra, but those of the D-*galacto*, D-*gluco*, and D-*talo* isomers have been analysed and are described herewith. The chemical shifts and coupling constants are listed in Tables I and II, respectively.

The three isomers represent three different conformational types (Fig. 1). The planar zigzag form of the D-*galacto* isomer has no parallel 1,3-interaction between the acetoxyl groups on C-3 and C-5, or C-4 and C-6. Hence the zigzag form (**1**) is

TABLE I

CHEMICAL SHIFTS ($\delta$) OF PENTA-ACETOXY-*trans*-1-NITRO-1-HEPTENES IN CHLOROFORM-*d*

| *Isomer* | *H-1* | *H-2* | *H-3* | *H-4* | *H-5* | *H-6* | *H-7* | *H-7'*[a] |
|---|---|---|---|---|---|---|---|---|
| D-*galacto* | 6.95 | 7.06 | 5.76 | 5.41 | 5.47 | 5.39 | 4.38 | 3.96 |
| D-*gluco* | 6.96 | 7.15 | 5.59 | 5.30 | 5.33 | 5.00 | 4.19 | 4.03 |
| D-*talo* | 7.21 | 7.40 | 5.79 | 5.34 | 5.42 | 5.41 | 4.30 | 3.93 |

[a]The proton resonating at higher field is designated as H-7'.

*Present address: Centre de Recherches sur les Macromolécules Végétales (CNRS), Cedex 53, 38 Grenoble Gare, France.

TABLE II

COUPLING CONSTANTS (IN Hz) OF PENTA-ACETOXY-*trans*-1-NITRO-1-HEPTENES IN CHLOROFORM-*d*

| *Isomer* | $J_{1,2}$ | $J_{2,3}$ | $J_{1,3}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{5,6}$ | $J_{6,7}$ | $J_{6,7'}$ | $J_{7,7'}$ |
|---|---|---|---|---|---|---|---|---|---|
| D-*galacto* | 13.1 | 4.6 | −1.7 | 2.0 | 9.9 | 1.8 | 4.9 | 7.6 | −11.7 |
| D-*gluco* | 13.3 | 4.8 | −1.7 | 6.2 | 3.0 | 7.3 | 2.7 | 5.7 | −12.5 |
| D-*talo* | 13.3 | 5.1 | −1.9 | 2.4 | 9.2 | 2.3 | 5.3 | 7.3 | −11.4 |

expected to be the most-stable conformer; the n.m.r. spectrum indicates that the compound in solution is almost wholly in this conformation (the expected coupling constants being $J_{3,4}$ 2, $J_{4,5}$ 9, and $J_{5,6}$ 2 Hz). The D-*talo* isomer has a parallel 1,3-interaction between O-3 and O-5 in the planar zigzag form. There is only one conformation free of such interaction: the "sickle"[4] (**2**), formed from the zigzag form by a 120° rotation around the C-3–C-4 bond. The coupling constants expected for this conformation are $J_{3,4}$ 2, $J_{4,5}$ 9, and $J_{5,6}$ 2 Hz, and the good agreement with prediction shows that the compound in solution is almost wholly in this "sickle" conformation.

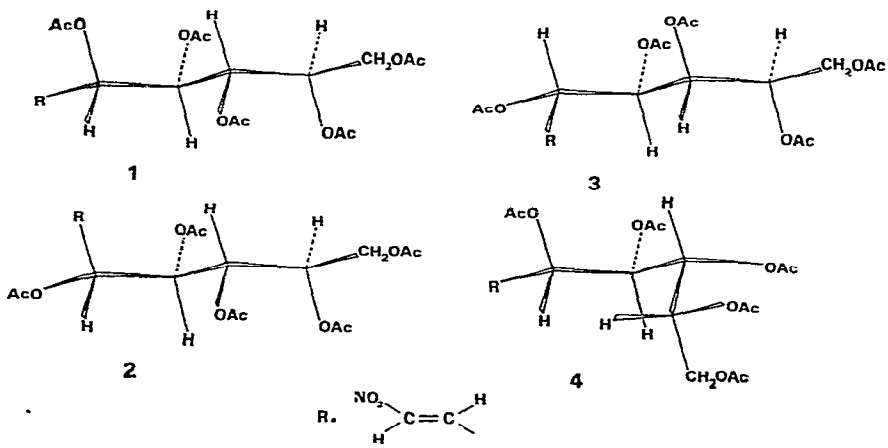


Fig. 1. Main conformations in solution for **1**, D-*galacto* isomer; **2**, D-*talo* isomer; **3** and **4**, D-*gluco* isomer.

The D-*gluco* isomer also has a parallel 1,3-interaction between O-3 and O-5 in the planar zigzag form. There are two conformations free of such interactions: one (**3**) formed by a rotation of 120° around the C-3–C-4 bond; and one (**4**) formed by two such rotations around the C-4–C-5 and C-5–C-6 bonds[1]. The former conformer, with one *gauche* arrangement, is expected to be more stable than the latter, with two. The expected coupling constants are $J_{3,4}$ 9, $J_{4,5}$ 2, and $J_{5,6}$ 9 Hz for **3**; 2, 9, and 2 Hz for **4**; and 2, 2, and 9 Hz, respectively, for the zigzag form. The observed coupling constants show that the predominant conformer is **3** accompanied by significant amounts of **4** and, probably, by a small amount of the zigzag conformer. The behav-

iour of the three nitro compounds is therefore in accordance with results[3] obtained on other acyclic sugar derivatives.

The large values of $J_{1,2}$ indicate that the configuration of the olefinic bond is *trans* in all the three compounds[2,5].

## EXPERIMENTAL

The nitro compounds were obtained from Dr. M. B. Perry[6]; additional amounts were synthesized by the described methods[6,7].

The n.m.r. spectra were measured at 100 MHz with a Varian HA-100 spectrometer with tetramethylsilane as the lock signal and internal standard. Only the spectrum of the *gluco* isomer could be fully analysed. By courtesy of Thomson-CSF, 250-MHz spectra of the other isomers were run on their TSN-250 spectrometer; these spectra were amenable to full analysis.

In every spectrum, the signals of H-1 and H-2 at lowest field and those of H-7 and H-7′ at highest field (apart from the acetyl resonances) were well separated and amenable to first-order analysis as the AB parts of ABX systems.

In the spectrum of the *gluco* isomer, the couplings $J_{1,3}$ and $J_{2,3}$ are easily recognized in the multiplet at $\delta$ 5.6; this is therefore assigned to H-3 and provides a tentative value for $J_{3,4}$. Similarly, the multiplet at $\delta$ 5.0 is identified as the signal of H-6 and provides a value for $J_{5,6}$. The 2-proton multiplet at $\delta$ 5.3 therefore represents H-4 and H-5.

The LAOCOON III program was used for simulating the spectra. First, the four-spin sub-spectrum H-3–H-6 was calculated, keeping $\delta_3$ and $\delta_6$ constant during the iterations. The provisional parameters thus obtained were used to calculate two sub-spectra, one covering H-1 to H-6 and the other covering H-3 to H-7′. (The computer used could not handle the LAOCOON program for 8 spins.) The two sub-spectra obtained provided a good fit with the experimental spectrum (the H-6 part of the first and the H-3 part of the second being disregarded), and the H-4–H-5 multiplets of the two sub-spectra were exactly superposable, vindicating the method used for the calculations.

The spectrum of the *talo* isomer was similarly treated. In this case, however, the signals of H-4, H-5, and H-6 overlapped in the 100-MHz spectrum and provided insufficient data for iteration. In the 250-MHz spectrum, the high-field part of this multiplet showed as a pair of doublets, one splitting being identical with $J_{3,4}$; this was therefore taken as the signal of H-4 and provided provisional values of $J_{4,5}$ and $\delta_4$. The two six-spin sub-spectra were calculated as above and gave a good fit of the H-4–H-6 multiplet in the 250-MHz spectrum.

In the 100-MHz spectrum of the *galacto* isomer, the signals of H-4, H-5, and H-6 also overlap. The 250-MHz spectrum allows the recognition of H-5 as a pair of doublets on the low-field site of this multiplet. Two six-spin sub-spectra were again calculated, but because of the poor resolution of H-4 and H-6 precise iteration was difficult, and despite many iterations the tabulated results are considered to have a possible error of $\pm$0.3 Hz.

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REFERENCES

1 Part II: S. J. ANGYAL, R. LE FUR, AND D. GAGNAIRE, *Carbohyd. Res.*, 23 (1972) 121.
2 J. M. WILLIAMS, *Carbohyd. Res.*, 11 (1969) 437.
3 P. L. DURETTE AND D. HORTON, *Advan. Carbohyd. Chem. Biochem.*, 26 (1971) 49.
4 D. HORTON AND J. D. WANDER, *Carbohyd. Res.*, 10 (1969) 279.
5 W. BRÜGEL, TH. ANKEL, AND K. KRÜCKEBERG, *Z. Elektrochem.*, 64 (1960) 1121.
6 C. F. GIBBS, D. T. WILLIAMS, AND M. B. PERRY, *Can. J. Chem.*, 47 (1969) 1479; M. B. PERRY AND A. C. WEBB, *ibid.*, 46 (1968) 2481.
7 J. C. SOWDEN AND R. SCHAFFER, *J. Amer. Chem. Soc.*, 73 (1951) 4662; J. C. SOWDEN AND H. O. L. FISCHER, *ibid.*, 69 (1947) 1048.