Conformations of Some Acetylated Aldopyranosyl Halides

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A comparative study of the nuclear magnetic resonance (n.m.r.) spectra of eight acetylated aldopyranosyl halide derivatives,* each in the thermodynamically more stable anomeric form,[1] has shown that the favoured conformation of each compound in chloroform solution is that in which the halogen atom is axial.

The Table lists n.m.r. data for the tri-*O*-acetyl-D-pentopyranosyl bromides with the β-D-*arabino* (I), β-D-*ribo* (II), and α-D-*xylo* (III) configurations; the tetra-*O*-acetyl-α-D-hexopyranosyl bromides with the D-*galacto* (IV), and D-*gluco* (V) configurations; and 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride (VI), 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl bromide hydrobromide (VII), and 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranosyl bromide[2] (VIII).

Nuclear magnetic resonance spectral data

Compound	Anomeric proton τ	$J_{1,2}$ (c./sec.)	Ac protons, τ (integral, protons)
(I)	3·25	3·5	7·86 (3), 7·91 (3), 7·98 (3)
(II)	3·57	3·0	7·85 (6), 7·98 (3)
(III)	3·30	4·0	7·89 (3), 7·92 (6)
(IV)	3·23	3·5	7·86 (3), 7·91 (3), 7·97 (3), 8·01 (3)
(V)	3·68	3·5	7·83 (3), 7·93 (3), 7·99 (6)
(VI)	3·75	3·5	7·92 (3), 7·96 (3), 7·99 (3)
(VII)	2·86	3·5	7·77 (3), 7·91 (3), 7·94 (3)
(VIII)[2]	3·40	3·5	7·89 (3), 7·93 (6), 8·15 (3)

In each compound the anomeric proton (H–1) signal was observed at low field, and was separated from the next lowest ring proton signal by 0·75—1·5 p.p.m. Compounds (VI), (VII), and (VIII) showed additional signals at lower field than H–1. The NH proton in (VI) was observed at τ 3·28 as a unit-proton doublet, $J = 9{\cdot}0$ c./sec., which disappeared on deuteration. The NH_3^+ proton signal of (VII) was observed as a broad three-proton triplet at τ 1·38. The spectrum of (VIII) showed, in addition to aromatic signals in the region τ 0·9—1·8, a unit proton doublet, τ 2·84, $J = 10{\cdot}0$ c./sec., assigned to the NH proton.

The anomeric proton signal of each compound appeared as a doublet, $J_{1,2} = 3{\cdot}0$—$4{\cdot}0$ c./sec. This indicates[3,4] a projected angle between the C–1 and C–2 carbon–hydrogen bonds of about 60°, and excludes the possibility of a 1,2-*trans*-diaxial arrangement of protons. The doublets were sharply resolved, indicating a high degree of conformational purity in solution, in all examples except (II). The small $J_{1,2}$ value indicates that the favoured conformation of (II) is 1*C* as depicted, and not the alternate *C*1 conformation. This conformational assignment is further supported by the appearance of two of the acetoxy-group signals at low field, indicative[4,5] of the axial orientation. The incomplete resolution of the H–1 signal suggests that (II) may be conformationally less stable than the other compounds, and the possibility of a non-chair conformation cannot be excluded entirely.

The spectra of (I) and (IV) are closely similar in the region τ 3·0—5·2. Quartets at τ 4·89 and 4·93, respectively, can be assigned to H–2, with $J_{1,2} = 3{\cdot}5$ c./sec., $J_{2,3} = 10{\cdot}0$ c./sec. The acetoxy signal at τ 8·01 in (IV) can be assigned[4] to the 6-acetoxy-group; the pattern of the other three acetoxy

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* Spectra were measured with a Varian A60 n.m.r. spectrometer and analysed on a first-order basis. The crystalline compounds were freshly prepared by standard methods and were used in deuterochloroform solution, with tetramethylsilane as the internal reference. The probe temperature was approximately 30° C.

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[2] D. Horton, *J. Org. Chem.*, 1964, **29**, 1776.

[3] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

[4] L. D. Hall, *Adv. Carbohydrate Chem.*, 1964, **19**, 51.

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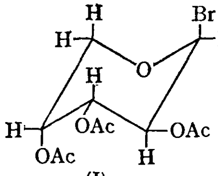
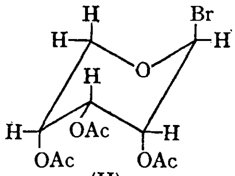
signals is identical for (I) and (IV), and the τ 7·86 signals can be assigned to axial acetoxy-groups at C–4. These results fully support the expected *C*1 conformation for (IV), and establish that the 1*C* conformation shown for (I) is the favoured conformation.

All multiplets in the spectrum of (III) are fully resolved. The C–2 proton is observed at τ 5·14 as a quartet, $J_{1,2} = 4{\cdot}0$ c./sec., $J_{2,3} = 10{\cdot}0$ c./sec., and the C–3 proton is observed as a triplet, τ 4·36, $J_{2,3} = J_{3,4} = 10{\cdot}0$ c./sec. Corresponding multiplets, with similar splitting patterns, are observed in the spectrum of (V). These results prove that the favoured conformation of (III) is the *C*1 conformation shown, and verify the expected *C*1 conformation of (V).

The predicted favoured conformation of (VI), (VII), and (VIII) is the *C*1 conformation shown. This is verified by analysis of the splitting patterns of the ring proton signals in comparison with the spectra of (III) and (V). The small $J_{1,2}$ coupling constants thus indicate that the H–1 proton is equatorial and the halogen atom is axial. This provides independent physical proof that (VI), (VII), and (VIII) have the α-D-configuration, as previously assigned on the basis of optical rotatory data.



(I)



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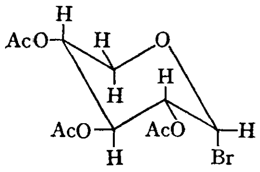
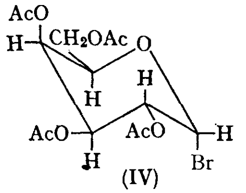


(III)



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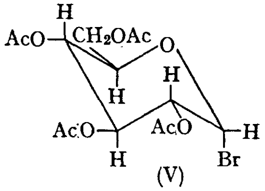
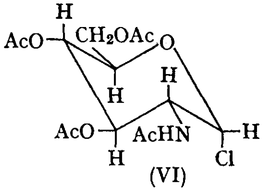
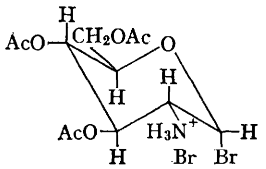


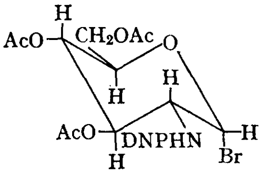
(V)



(VI)



(VII)



(VIII)

(*Received, February* 18*th*, 1965.)