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Note

Sucrose octa-acetate: the complete analysis of the ^{1}H-n.m.r. spectrum

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The ^{1}H-n.m.r. spectra of solutions of sucrose octa-acetate in benzene-d_6, chloroform-d, and acetone-d_6 at 100 MHz and 220 MHz have been studied by Binkley, Horton, and Bhacca[1]. Only the lowest-field parts (δ 5–6) of the spectra were analysed, *i.e.*, the chemical shifts of H-1,2,3,4 of the D-glucopyranosyl moiety and H-3′,4′ of the D-fructofuranosyl moiety, as well as their mutual coupling constants. At 300 MHz and using homo-INDOR, it is possible to unravel the whole spectrum.

The ^{1}H-n.m.r. spectral data for the solutions of sucrose octa-acetate in benzene-d_6, chloroform-d, and acetonitrile-d_3 are given in Table I, and in Figs. 1 and 2. Final spectral assignments were substantiated by homo-INDOR experiments at 300 MHz.

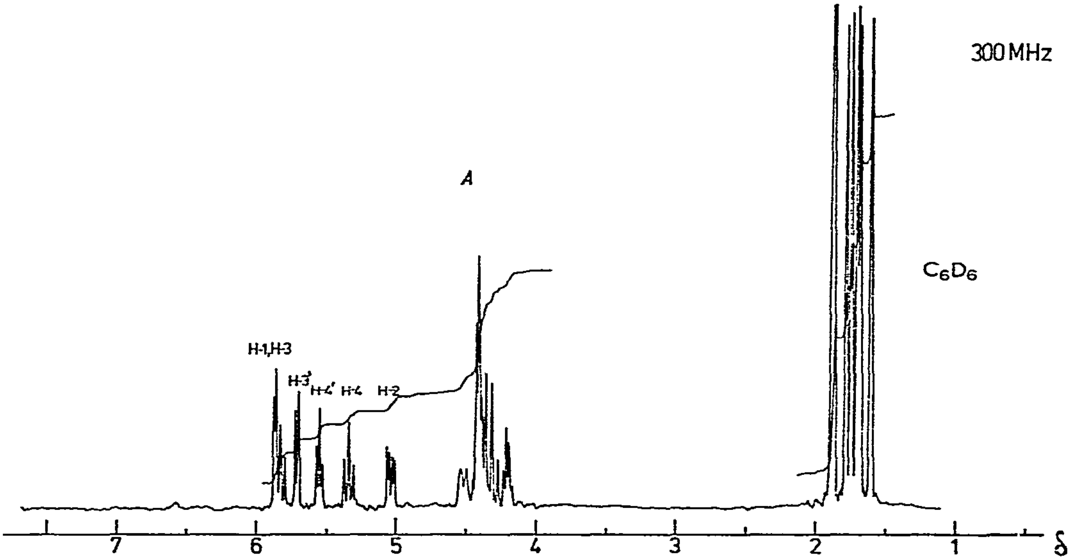

Fig. 1. ^{1}H-N.m.r. spectrum of sucrose octa-acetate in benzene-d_6 at 300 MHz.

TABLE I

^{1}H-N.M.R. DATA FOR SUCROSE OCTA-ACETATE AT 300 MHz[a]

D-*Glucosyl moiety*

Solvent	*H-1*[b]	*H-2*[b]	*H-3*[b]	*H-4*[b]	*H-5*	*H-6a*	*H-6b*	$J_{1,2}$[b]	$J_{2,3}$[b]	$J_{3,4}$[b]	$J_{4,5}$[b]	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
Benzene-d_6	5.85	5.02	5.81	5.33	4.51	4.40	4.36	3.6	10.3	9.6	10.0	4.7	2.6	−12.2
Chloroform-d	5.69	4.87	5.45	5.08	4.30	4.28	4.15	3.6	10.4	9.2	9.6	4.2	2.4	−12.3
Acetonitrile-d_3	5.64	4.86	5.38	5.03	4.24	4.18	4.09	3.6	10.4	9.0	9.8	4.8	2.4	−12.4

D-*Fructosyl moiety*

Solvent	*H-1'a*	*H-1'b*	*H-3'*[b]	*H-4'*[b]	*H-5'*	*H-6'a*	*H-6'b*	$J_{1'a,1'b}$	$J_{3',4'}$[b]	$J_{4',5'}$[b]	$J_{5',6'a}$	$J_{5',6'b}$	$J_{6'a,6'b}$
Benzene-d_6	4.37	4.28	5.70	5.54	4.19	4.41	4.41	−12.0	5.5	5.8	—	—	—
Chloroform-d	4.14	4.14	5.45	5.36	4.22	4.36	4.31	—	5.6	6.1	4.5	6.5	−11.8
Acetonitrile-d_3	4.21	4.17	5.44	5.32	4.21	4.29	4.22	−12.0	5.6	6.0	5.0	6.6	−12.3

[a] Shifts are in p.p.m. from Me_4Si as the internal standard; coupling constants in Hz. [b] Also reported and in agreement with data cited in ref. 1 for chloroform-d and benzene-d_6.

The extracted parameters were then refined through SIMEQ 16/II simulations until there was agreement between simulated and experimental patterns.

With benzene-d_6 as solvent, the resonances of H-5 (glucose moiety) and H-5′ (fructose moiety) are well separated from the complex pattern formed by the two AB parts of the ABX systems resulting from the protons at C-5 and C-6 of each of the two rings, together with the AB spin-system of H-1′a and H-1′b. These ABX parts may be considered as separate entities, in which the X part shows a further first-order coupling with H-4 or H-4′, because the signals for H-4,5 and H-4′,5′ are separated by at least (in acetonitrile-d_3) 443 Hz at 300 MHz. Thus, in benzene-d_6, the signals for H-5′ and H-5 are found at δ 4.18 and 4.41, respectively (Fig. 2*A*). The distance

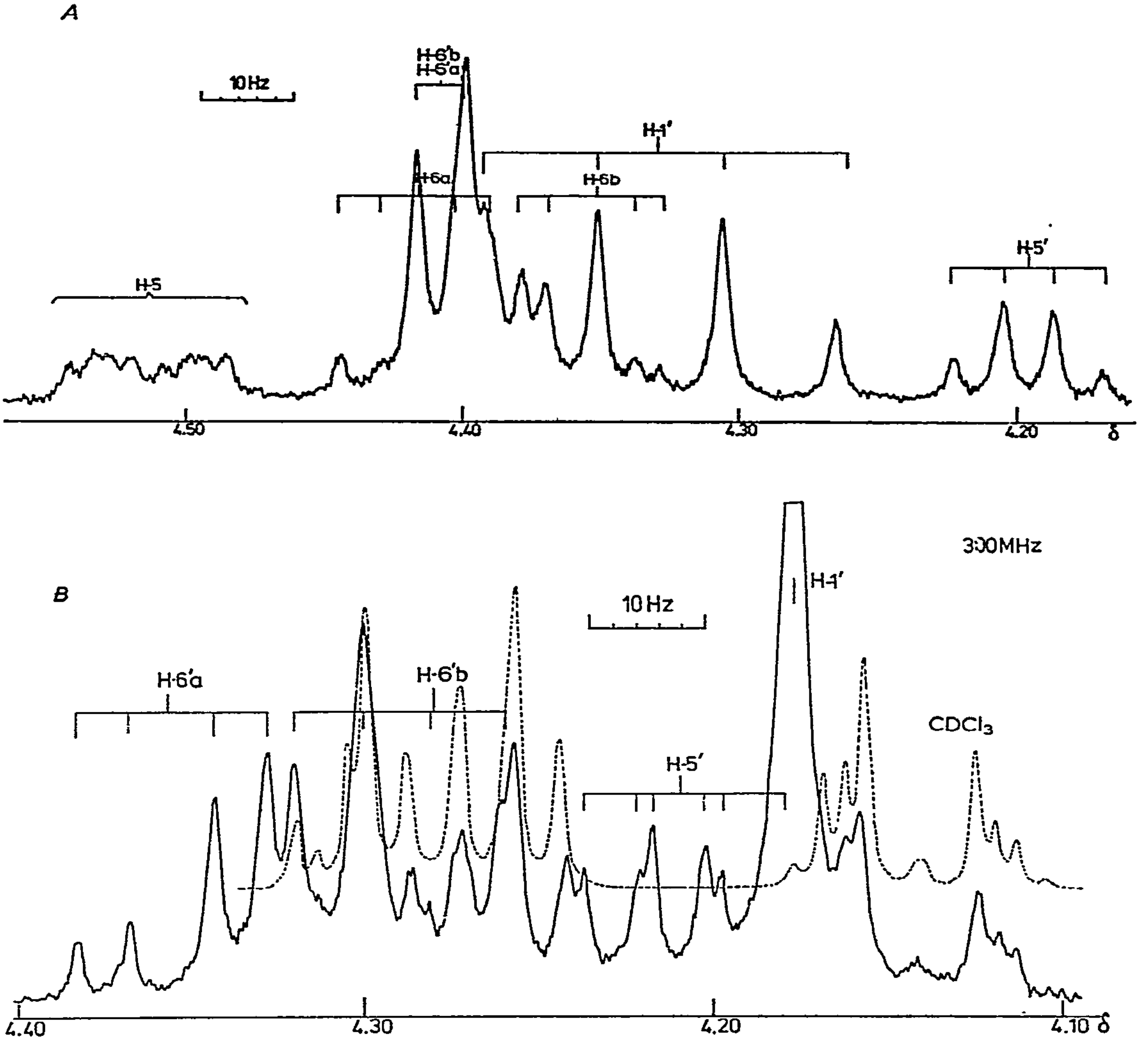

Fig. 2.

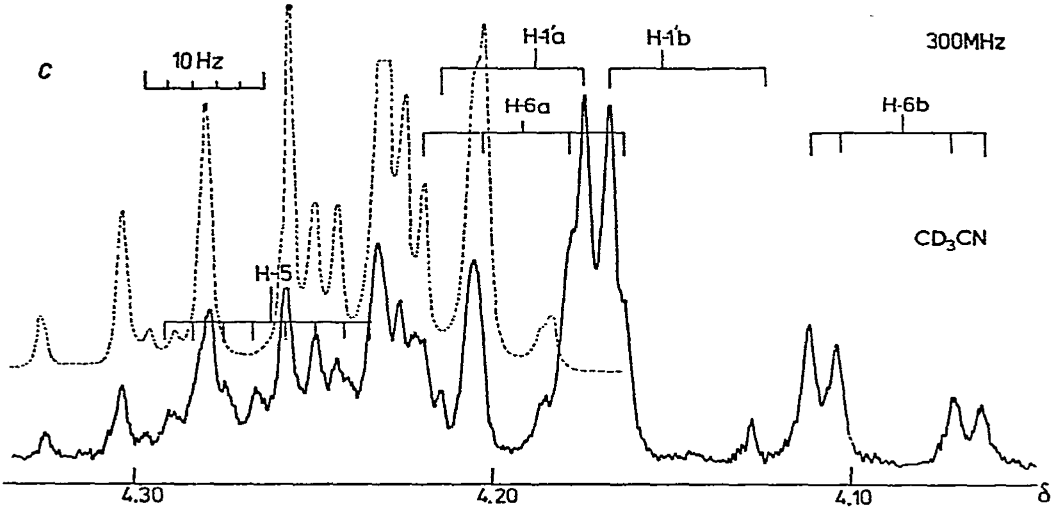

Fig. 2. ^{1}H-N.m.r. spectrum of sucrose octa-acetate at 300 MHz. Extended pattern at δ 4.1–4.5 (100-Hz sweepwidth): *A*, in benzene-d_6; *B*, in chloroform-*d* [the upper spectrum (dotted lines) is the simulated spectrum of H-5,6a,6b of the D-glucopyranosyl moiety]; *C*, in acetonitrile-d_3 [the upper spectrum (dotted lines) is the simulated spectrum of H-5',6'a,6'b of the D-fructofuranosyl moiety]. In *B* and *C*, the intensities of the experimental and simulated spectra are different.

between the outer lines of the resonances for H-5 is 17.2 Hz, being almost the sum of $J_{4,5}$ (10 Hz), $J_{5,6a}$ (4.7 Hz), and $J_{5,6b}$ (2.6 Hz), as can be derived from first-order inspection. In all the solvents, the values for $J_{5,6a}$ and $J_{5,6b}$ are very similar and also close to those found[2] for a solution of α-D-glucopyranose penta-acetate in chloroform-*d*. In the region δ 4.3–4.45 for the solution in benzene-d_6, only two lines of the AB part (H-6'a and H-6'b) of the ABX spin-system of the D-fructofuranosyl moiety are visible. After abstraction of the value (5.4 Hz) of $J_{4',5'}$ in the X part (H-5'), there remains an apparent triplet with identical linewidths, although only the value of the sum (10.8 Hz) of $J_{5',6'a}$ and $J_{5',6'b}$ can be advanced with certainty. Here it seems to be reasonable to accept that the equal values for the individual couplings (*e.g.*, $J_{5',6'a} = J_{5',6'b} = 5.4$ Hz) must be very close to the real values, since they are close to the magnitudes of the parameters found in the other solvents.

In chloroform-*d*, the ABX system formed by H-5' (A) and H-6'ab (B and X) of the D-fructofuranosyl moiety may be readily picked out of the very confused pattern by homo-INDOR experiments. From sub-spectral analysis, it was determined that $J_{5',6'a}$ and $J_{5',6'b}$ were 4.5 and 6.5 Hz, respectively. In this solvent, H-5,6a,6b of the D-glucopyranosyl moiety formed a more complex ABC system that could only be analysed with computer-aided simulations.

With acetonitrile-d_3, the signals for H-5,6a,6b appear as an ABX system very similar to the one encountered in benzene-d_6, but H-5',6'a,6'b of the D-fructofuranosyl ring appear as an ABC system, again analysed by computer-aided simulations. The values extracted for $J_{5',6'a}$ and $J_{5',6'b}$ are different from those reported by Binkley, Binkley, and Grey[3] for the di-D-fructose dianhydrides. However, from inspection of the values[1,3] of $J_{3',4'}$ and $J_{4',5'}$, it follows that the conformation of the D-fructofuranosyl rings must be different. Because these values are similar in the solvents studied, we can conclude that it is the conformation of the furanoid system that controls the averaged rotameric populations around the C-5′–C-6′ bond.

From inspection of the region δ 4–4.5, it was possible to locate the signals of H-1′a and H-1′b of the D-fructofuranosyl moiety, although they are isochronous in chloroform-*d*. When the chemical shifts in chloroform-*d* are compared with those in benzene-d_6, an averaged upfield-shift of ~0.15 p.p.m. is generally observed, whereas a slight downfield-shift is observed for H-5′. The same relationship holds in comparing the values obtained in acetonitrile-d_3 and benzene-d_6, with an averaged upfield-shift of 0.23 p.p.m., except for H-5′.

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