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Note

A ^{1}H-n.m r. study of D-fructose in D_2O

ANDRE DE BRUYN, MARC ANTEUNIS, AND GEORGES VERHEGGE
Chemistry Department, Laboratory for NMR Spectroscopy, State University of Ghent, Krijgslaan 271 (S4bis), Ghent (Belgium)
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D-Fructose in D_2O has been studied by ^{13}C-n m r spectroscopy[1 2] and the hydroxyl-proton resonances in methyl sulphoxide have been examined[2] From the ^{13}C-n m r data, it was concluded[1,2] that D-fructose exists in water as an equilibrium of the β-pyranose, β-furanose, α-furanose, and α-pyranose in the ratios of 6 3 1 traces, whereas in methyl sulphoxide the ratios were 1 3 1 3 traces

Using ^{1}H-n m.r spectroscopy at 300 MHz, we have determined completely the spectrum of the most abundant isomer (**1**) of D-fructose in D_2O, namely the D-fructopyranose form The data are shown in Table I and Fig 1 Isomer **1** occurs in the *1C*(D) form

TABLE I

^{1}H-N M R SPECTRAL DATA OF THE TWO MAJOR ISOMERS OF D-FRUCTOSE IN D_2O

	Chemical shifts (δ p p m)						
	H-1	*H-1'*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*
Major isomer (**1**)	3 71	3 57	3 80	3 89	3 99	4 03	3 71
Second isomer (**2**)	3 59	3 56	∼4 11	∼4 11	—	—	—
	Coupling constants (Hz)						
	$J_{1\,1}$	$J_{3,4}$	$J_{4\,5}$	$J_{5\,6}$	$J_{5\,6}$	$J_{6\,6}$	
1	−11 8	10 0	3 2	1 3	1 8	−12 4	
2	−12 2	(∼0)	(∼0)	—	—	—	

From a previous study[3], it was concluded that the chemical shifts of H-3 and H-4 of fructofuranosyl moieties are found below δ 3 95 p p m As this is not the case for **1**, a pyranoid ring is indicated The fact that H-5 resonates at a lower field than do H-3 and H-4 indicates that the former might be *eq*, both other protons being *ax* in the *1C*(D) form of fructose The value (10 0 Hz) of $J_{3\,4}$ indicates an antiperiplanar

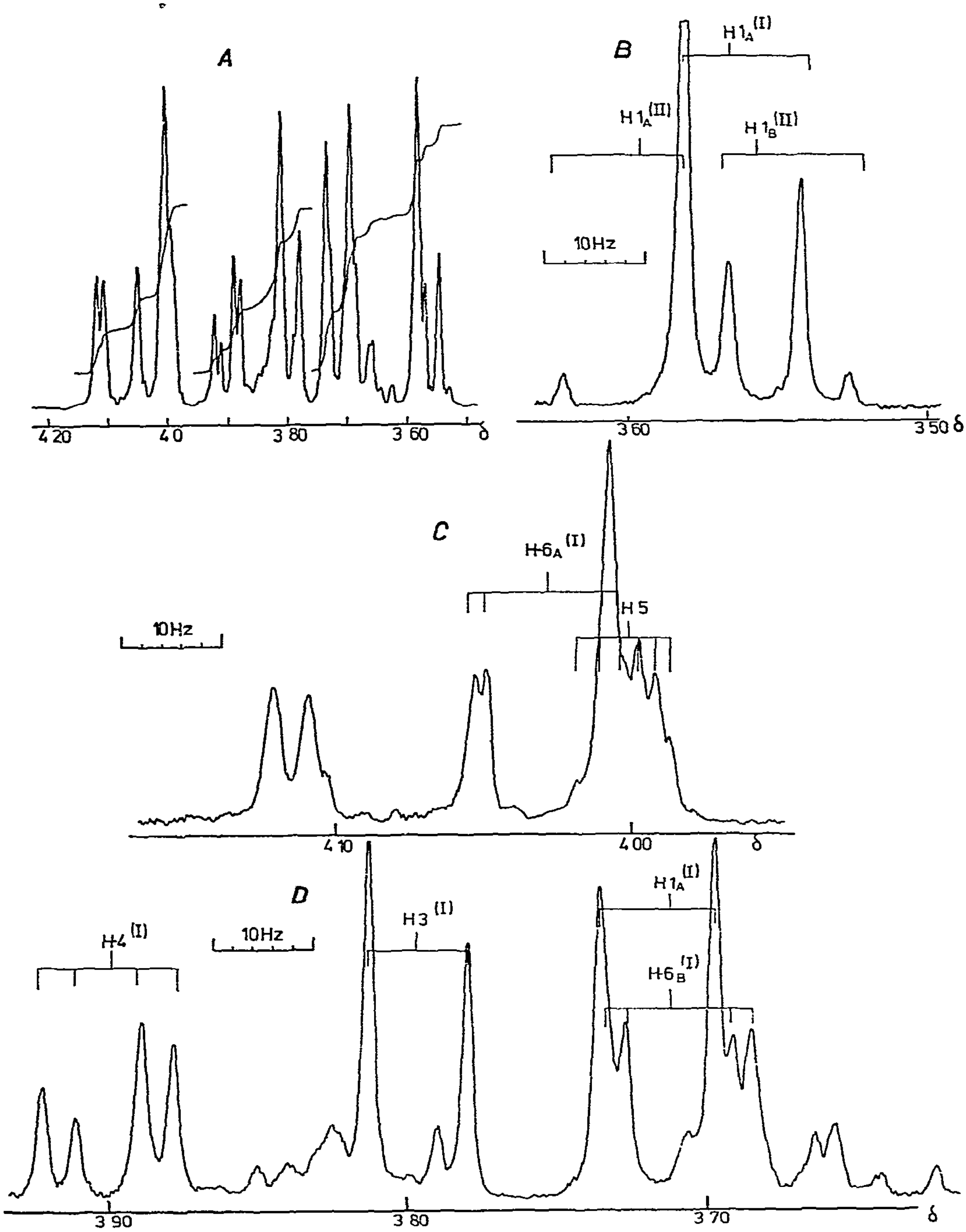

Fig 1 ^{1}H-N m r spectrum of D-fructose at 300 MHz in D_2O at 500- (*A*) and 100-Hz sweep-width (*B–D*), 1 (I)major isomer, 2 (II)second isomer configuration of H-3 and H-4 The value (1 3 Hz) for $J_{5,6}$ is typical[5] of an *eq–eq* relationship, when one of the protons is antiperiplanar with a substituent bearing lone pairs of electrons The values of 3 2 and 1 8 Hz for $J_{4\ 5}$ and $J_{5\ 6'}$ seem to be typical for an *ax–eq* relationship having two and one substituents, respectively, in an antiperiplanar position (considering the ring oxygen as a substituent) These data were confirmed by INDOR experiments at 100 MHz, subsequently refined by simulations with a SIMEQ 16/II programme

For the isomer **2**, only the position of H-1,1′ can be assigned with precision, as well as J_{gem} However, the remaining shift parameters are consistent with a furanoid ring The doublet-like pattern at δ 4 11 integrates for two protons, and their position at a field lower than 3 95 p p m is an indication[3] that they might be H-3 and H-4 of a furanoid ring Because of the pronounced degeneration of the pattern at $\delta \sim 4$ 1 and overlap with the signal for H-6 of **1** at 100 MHz, no precise homo-INDOR experiments were possible, although it is clear that responses ascribed to H-5 and, presumably, H-6 in **2** are located higher field than 3 9 p p m , as are the resonances of H-5 in fructofuranosyl-containing disaccharides We can assume that the doublet-like structure is due to two singlets, where $J_{3,4} \approx J_{4\ 5} \approx 0$ Hz The resulting dihedral angles[6] are H-3/H-4 ≈ H-4/H-5 ≈ 78°, which are typical for a furanoid ring in a time averaged, flattened E_4 conformation, for which the theoretical angle is 70° As shown by Perlin[2], a hydrogen bond occurs between HO-1 and probably HO-4, a surmise based on a comparison with the HO spectrum of lactulose In this case, the E_4 or $^3T_4$ conformation is expected

There is no ^{1}H-n m r proof of the α or β configuration of **1** or **2** From other techniques, however, it is obvious that both must be β-D isomers[2 7] The ^{1}H-n m r spectra obtained for solutions of D-fructose in methyl sulphoxide-d_6 or methyl sulphoxide-d_6 + trifluoroacetic acid also did not allow analysis of the D-fructofuranose form, although an increased intensity of the doublet-like pattern at low field suggests the occurrence of a substantially larger proportion of this form

EXPERIMENTAL

The 300-MHz spectrum was recorded on a Varian HA 300 instrument, and INDOR experiments were performed at 100 MHz on a Varian HA 100 spectrometer, using 10% solutions with sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate as internal standard

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