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Note

Application of c.m.r. spectroscopy to the problem of the anomeric configuration of the di-D-fructose dianhydrides

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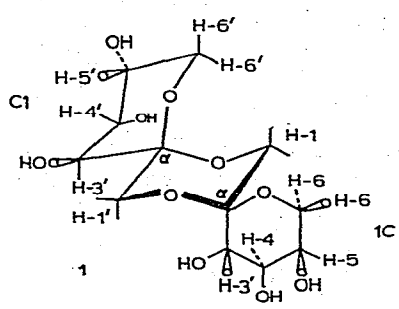
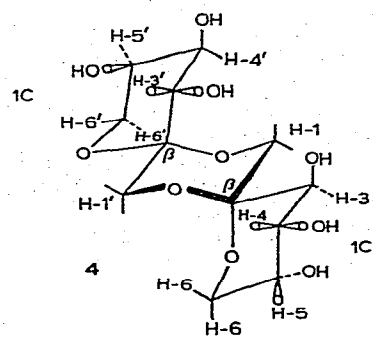
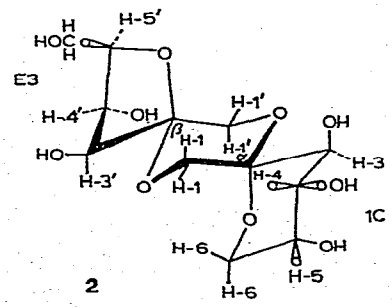
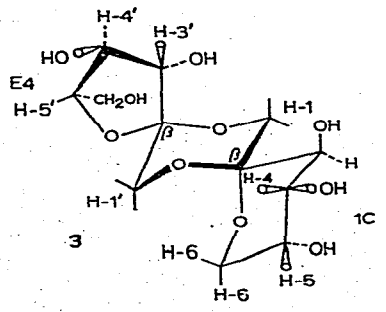
With the determination of the conformations of the ring systems in the di-D-fructose dianhydrides (previously[1] designated diheterolevulosans I–IV) (**1–4**), only the anomeric configurations were lacking to complete the structural assignments for









these compounds. Application of Hudson's isorotation rules[2] to the optical rotatory data obtained from **1**–**4** strongly suggested that **1** and **4** were α,α and β,β anomers, respectively[3e]; these rules also indicated that the pyranose moieties in **2** and **3** were related as anomers[3d]. Carbon-13 magnetic resonance (c.m.r.) spectroscopy is here applied to the problem of the structural assignments for compounds **1**–**4**.

RESULTS AND DISCUSSION

The c.m.r. spectra of the di-D-fructose dianhydrides **1**–**4** are shown in bar-graph form in Fig. 1 and the chemical-shift data are presented in Table I. Each spectrum displays two absorptions in the lower-field, anomeric region[4] (95–103 p.p.m., the signal for **4** has double intensity). Further upfield, in the furanose-carbon region[5,6] (76–84 p.p.m.), compounds **2** and **3** show absorptions. Finally, still further upfield, in the pyranose-carbon region[5] (64–72 p.p.m.), all four compounds exhibit absorptions. These spectra confirm the general structural assignments made to these systems from chemical degradative studies, namely, that the sugar moieties in **1** and **4** have pyranoid ring-systems only, whereas both pyranoid and furanoid ring-structures are present in **2** and **3**.

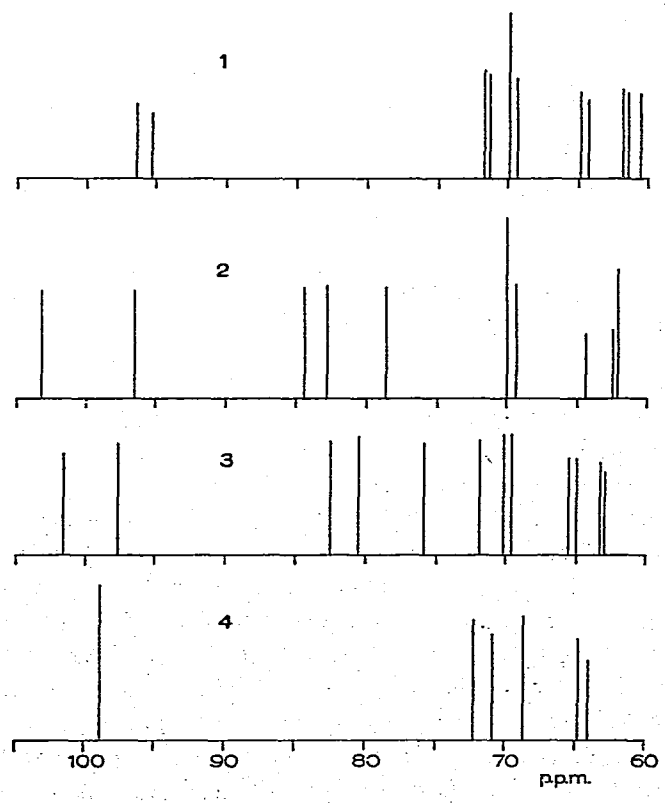


Fig. 1. C.m.r. spectra of the di-D-fructose dianhydrides (**1**–**4**).

TABLE I

C.M.R. CHEMICAL SHIFTS OF DI-D-FRUCTOSE DIANHYDRIDES (DIHETEROLEVULOSANS) I (1), II (2), III (3), AND IV (4)[a]

Assignment[b]	*Chemical shift of* ^{13}C *resonances of*			
	1[c]	2[c]	3[c]	4
C-2				
β-D-Fructofuranose		103.0	101.5	
β-D-Fructopyranose			97.6	98.8
				98.8
α-D-Fructopyranose	96.2	96.4		
	95.1			
C-3, C-4, C-5		84.2	82.5	
β-D-Fructofuranose		82.7	80.5	
		78.5	75.8	
C-3, C-4, C-5	71.4		71.8	72.2
D-Fructopyranose	71.2			72.2
	69.7	69.8	70.1	70.8
	69.7	69.8		70.8
	69.2	69.3	69.7	68.7
	64.6			68.7
C-1, C-6			65.5	64.8
			64.9	64.8
	64.2	64.2	63.2	64.1
			63.0	64.1
		62.3		
	61.6	62.0		
	61.3	62.0		
	60.4			

[a]Chemical shifts are expressed in p.p.m. downfield of the ^{13}C resonance of Me_4Si. [b]Except for the anomeric-carbon assignments, these are tentative. [c]Measured in D_2O.

The most significant use of the c.m.r. spectra of di-D-fructose dianhydrides **1**–**4** is as an aid in the assignment of the configuration to the anomeric centers in these sugars; the usefulness of these data as such an aid is evaluated here.

1′,2-Anhydro-1-O-β-D-fructopyranosyl-(1C)-*β-D-fructopyranose*-(1C) (**4**).—Every peak in the c.m.r. spectrum of **4** was of two-carbon intensity. Relating these intensities to the assignment of configuration in **4**, both anomeric carbon atoms in the D-fructopyranose residues must be either α,α or β,β. As the resonances of the β-pyranose anomeric carbon atoms in D-fructose and turanose are observed at 98.9 and 98.5 p.p.m., respectively, and that of the anomeric carbon atom in **4** is at 98.8 p.p.m., comparison of the c.m.r. chemical shifts with these model systems supports the β,β assignment based on Hudson's isorotation rules. These data confirm unequivocally the full structural assignment to **4** as 1′,2-anhydro-1-*O*-β-D-fructopyranosyl-(*1C*)-β-D-fructopyranose-(*1C*).

1′,2-Anhydro-1-O-α-D-*fructopyranosyl*-(1C)-α-D-*fructopyranose*-(C1) (**1**). — As Hudson's isorotation rules indicate that the configuration at the anomeric centers in **1** is probably α,α, the presence of two closely associated signals in the anomeric region of the spectrum was surprising (the β,β anomer, **4**, exhibited one signal of double intensity in the anomeric region). However, n.m.r. studies have shown that the two D-fructopyranose moieties in **1** adopt different conformations (*C1* and *1C*). The occurrence of these two signals, strongly suggesting that the anomeric carbon atoms are in different environments, is thus understandable. Interpretatation of this spectrum was made even more difficult by the unavailability of a suitable model compound for α-D-fructopyranose. The signals from the anomeric carbon atoms in **1**, at 96.2 and 95.1 p.p.m., are significantly upfield from those of the β-D-fructopyranose residue in **4**, in turanose, and in D-fructose (98.5–98.9 p.p.m.). Although the support is somewhat less direct for **1** than for **4**, the c.m.r. chemical-shift data fully support the evidence from Hudson's isorotation rules that lead to the assignment for **1** of the structure 1,′2-anhydro-1-*O*-α-D-fructopyranosyl-(*1C*)-α-D-fructopyranose-(*1C*).

1′,2-Anhydro-1-O-α-D-*fructopyranosyl*-(1C)-β-D-*fructofuranose*-(E3) (**2**). — The absolute anomeric configuration of the D-fructofuranose moieties in sucrose, 1-kestose, and nystose has been determined to be β by neutron diffraction and X-ray crystallography[7]. The ^{13}C chemical shifts of the anomeric carbon atoms in the β-D-fructofuranose moieties in these compounds are 103.4, 103.2–103.7, 102.8–103.7 p.p.m., respectively[5,6]. The signal furthest downfield in the anomeric region was observed at 103.0 p.p.m. and is assigned to the furanose moiety having the β-D configuration (this value is significantly different from those for the signals (105.0 and 105.2 p.p.m.) assigned to the D-fructofuranose moiety having the α-D anomeric configuration). The second anomeric-carbon absorption, at 96.4 p.p.m., was in close agreement with the anomeric-carbon shift-values found for the α-D-fructopyranose moiety in compound **1**. These data support the full structural assignment to **2** as 1′,2-anhydro-1-*O*-α-D-fructopyranosyl-(*1C*)-β-D-fructofuranose-(*E3*).

1′,2-Anhydro-1-O-β-D-*fructopyranosyl*-(1C)-β-D-*fructofuranose*-(E4) (**3**). — The c.m.r. spectrum of **3**, and the other c.m.r. data, indicate clearly that **3** possesses both pyranoid and furanoid ring-systems. The absorption at 101.5 p.p.m. is most probably that of the anomeric carbon atom of the β-D-fructofuranose moiety (the value of 101.3 p.p.m. was reported[5] for the anomeric carbon atom of a β-D-fructofuranose moiety of D-fructose in aqueous solution). The value of 101.5 p.p.m. is well separated from those signals (105.0 and 105.2 p.p.m.) attributed to the anomeric carbon atom of α-D-fructofuranose[5], and the assignment of the β-D configuration to the anomeric carbon atom in the D-fructofuranose moiety of **3** is therefore made. The other ^{13}C resonance (97.6 p.p.m.) in the anomeric region for **3** cannot be assigned with certainty. The application of Hudson's isorotation rules to **2** and **3** indicated that they possess anomeric D-fructopyranose residues. This fact, together with the c.m.r. data, favor the β-D configurational assignment for the anomeric carbon atom in the D-fructopyranose moiety of **3**. These data permit **3** to be tentatively assigned as 1′,2-anhydro-1-*O*-β-D-fructopyranosyl-(*1C*)-β-D-fructofuranose-(*E4*).

C.m.r. spectroscopy thus appears to be a useful aid for configurational assignment in the di-D-fructose dianhydrides, **1–4**; however, there are factors influencing the chemical-shift values that are not yet understood.

EXPERIMENTAL

Proton-noise-decoupled, c.m.r. spectra of the di-D-fructose dianhydrides **1–4** in deuterium oxide were recorded with a Varian XL-100-15 n.m.r. spectrometer fitted with a S-124XL/VFT-100X Fourier-transform accessory; spectra were recorded at 35° by using the deuterium resonance of deuterium oxide as the lock signal, and they are referenced to tetramethylsilane through internal 1,4-dioxane. Compounds **1–4** were prepared by published procedures[3].

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