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Note

Tautomeric equilibria of some sugars by partially relaxed, ^{13}C pulse Fourier-transform, nuclear magnetic resonance spectroscopy*†

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The objective of this work was to determine whether routine, ^{13}C-n.m.r. spectra can be used for accurate determination of tautomeric equilibria for sugars in solution. It is generally considered that integrated intensities from ^{13}C, pulse, Fourier-transform (p.F.-t.) n.m.r. spectra are not very reliable, quantitative measures of relative concentrations of compounds in admixture, because of the nuclear Overhauser effect and differences in the spin–lattice relaxation times (T_1) of different nuclei, as well as problems arising from inadequate, digital resolution of the spectra[2]. Several techniques have been developed to circumvent these difficulties. The nuclear Overhauser enhancement (n.O.e.) can be diminished by the addition of a paramagnetic species to the sample[3], although this method may not always be reliable[4]. Alternatively, a gated decoupling technique may be used for minimizing the Overhauser enhancement[5]. Saturation problems associated with excessive, radiofrequency power can be overcome by use of a suitable time-delay between pulses; the delay should be about 3–4 times the longest relaxation-time of any nucleus in the molecule if a 1:1 intensity correspondence is to be expected between signals of different atoms in a given molecule[6]. Application of the latter method results in considerable lengthening of the time required for recording spectra having an acceptable signal-to-noise ratio. For quantitative analysis of complex mixtures with samples of realistic size, this method leads to spectral accumulation-times that are prohibitively long. A third method[7], which retains the advantage of short recycling times, and also retains the nuclear Overhauser enhancement effect, ignores differences between nuclei in their spin–lattice relaxation-times and n.O.e., but ensures that the spectra are always obtained under conditions of equal (or near-equal) concentration, temperature, pulse width, and pulse-repetition (recycling) rate. By including a known amount of a suitable, standard compound

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in the mixture to be analyzed, the intensity of a standard resonance-peak can be compared with the intensities of each resonance in the spectrum. The amount of each component present in the mixture may then be determined from the concentration of the standard.

Nevertheless, it has been demonstrated[8], at least for such large, asymmetrical molecules as sugars, that the quality (signal-to-noise ratio and base-line stability) of ordinary p.F.-t., ^{13}C-n.m.r. spectra may be adequate for obtaining accurate integrals, because nearly all of the carbon atoms have the same n.O.e., and thus the same integrated intensities[8]. For example, most of the protonated carbon atoms in sucrose have relaxation times of <1 s. It would seem, therefore, that these relaxation times should be sufficiently short to make ordinary Fourier-transform, n.m.r. spectroscopy a sufficiently accurate, quantitative technique for the study of complex molecules, including sugars, without the need for the aforementioned special techniques.

The equilibrium compositions of tautomeric forms of various aldoses and ketoses, mostly in aqueous solution, have been studied by ^{13}C-p.F.-t., n.m.r. spectroscopy[9–22]. Long repetition-times of up to 2.8 s (ref. 16), delays between pulses[12] as long as 8 s, and long-term scans (up to 100,000) have been used[16]. We now demonstrate that even routine, partially relaxed, ^{13}C-p.F.-t., n.m.r. spectra can be used to provide reliable, quantitative data on tautomeric equilibria of sugars in solution.

EXPERIMENTAL

Proton-decoupled, natural-abundance-carbon-13, pulse Fourier-transform, n.m.r. spectra of D-glucose, D-mannose, D-fructose, and D-ribose (Pfanstiehl Labs. Inc., Waukegan, Illinois) were recorded by Dr. C. Cottrell with a Bruker HX-90 multinuclear spectrometer. Each sugar (0.4 g) was dissolved in 1.5 mL of D_2O (Stohler Isotope Chemicals, Inc., Waltham, Mass.), and spectra were recorded immediately after dissolution and again after mutarotation was complete. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was added as the internal reference, and all resonances were referenced to the highest-field, ^{13}C resonance of DSS; by using internal 1,4-dioxane (δ_c = 67.4 p.p.m. downfield from internal Me_4Si) as an additional reference, the aforementioned resonance of DSS was found to lie 1.6 p.p.m. upfield of the signal of Me_4Si, so that all chemical shifts originally referenced to DSS were appropriately recalculated. Spectra were recorded at $\sim 30°$ by using the deuterium resonance of D_2O as the lock signal. Measurements were made at a frequency of 22.63 MHz, with proton broad-band decoupling at 90 MHz. Typical conditions of measurement were as follows: sweep width 3–5 kHz; frequency of repetition (recycling) 0.8–1.0 s; and 8,000 data-points (16,000 for the mutarotated solution of D-fructose).

DISCUSSION

Table I shows ^{13}C-chemical shifts for tautomeric forms of D-glucose, D-

TABLE I

CARBON-13 CHEMICAL SHIFTS FOR TAUTOMERS OF D-GLUCOSE, D-MANNOSE, D-FRUCTOSE, AND D-RIBOSE IN SOLUTION

Tautomeric form	*Chemical shifts in p.p.m. downfield from Me_4Si*						*Ref.*
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	
D-Glucose							
α-pyranose	93.0	72.3	73.7	70.6	72.3	61.6	*a*
	93.0	72.5	73.8	70.6	72.3	61.8	*b*
	93.3	72.8	74.2	70.9	72.5	62.3	*c*
	94.9	71.2	72.6	69.4	71.2	60.4	*d*
	92.94	72.47	73.75	70.56	72.28	61.59	*e*
	93.48	72.95	74.26	71.09	72.76	62.26	*f*
β-pyranose	97.0	75.1	76.8	70.6	76.7	61.6	*a*
	96.8	75.2	76.7	70.6	76.7	61.8	*b*
	97.2	75.5	77.1	70.9	77.1	62.3	*c*
	95.7	74.0	75.6	69.4	75.6	60.6	*d*
	96.74	75.14	76.71	70.60	76.78	61.74	*e*
	97.28	75.63	77.21	71.09	77.21	62.28	*f*
D-Mannose							
α-pyranose	95.0	71.6	71.2	67.8	73.3	62.0	*a*
	94.9	71.7	71.3	67.9	73.2	62.0	*b*
	96.1	72.7	75.8	68.8	73.9	66.6	*c*
	93.9	70.6	70.1	66.7	72.2	60.9	*d*
	95.0	71.7	71.3	68.0	73.4	62.1	*g*
	95.42	72.16	71.75	68.31	73.70	62.51	*f*
β-pyranose	94.6	72.2	74.0	67.6	77.0	62.0	*a*
	94.4	72.0	74.1	67.6	76.7	62.0	*b*
	95.5	72.9	75.0	68.5	77.8	63.0	*c*
	93.5	71.1	72.9	66.4	76.1	60.9	*d*
	94.6	72.3	74.1	67.8	77.2	62.1	*g*
	95.05	72.66	74.50	68.11	77.37	62.51	*f*
D-Fructose							
α-pyranose	66.1	—	71.1	71.4	—	66.1	*a*
	66.1	—	71.5	71.1	—	66.1	*h*
	65.9	—	70.9	71.3	—	—	*i*
	65.9	99.1	70.9	71.3	70.0	66.1	*j*
	63.2	99.0	71.8	72.1	66.2	62.2	*k*
	65.9	99.1	70.9	71.3	62.0	61.9	*l*
β-pyranose	64.9	99.0	68.6	70.6	70.1	64.3	*a*
	64.91	98.89	68.57	70.78	70.16	64.24	*e*
	65.0	99.0	70.7	70.1	68.7	64.3	*h*
	64.3	99.3	70.7	68.6	70.2	64.9	*m*
	63.7	98.0	67.3	69.6	69.1	63.3	*d*
	64.7	99.1	68.4	70.5	70.0	64.1	*i*
	64.7	99.1	68.4	70.5	70.0	64.1	*j*
	65.6	99.1	69.3	71.1	70.4	64.6	*k*
	64.7	99.1	68.4	70.5	70.0	64.1	*l*
α-furanose	63.7	105.3	82.9	77.0	82.3	62.1	*a*
	63.94	105.23	82.96	77.02	82.16	62.08	*e*
	62.2	105.4	83.1	83.2	77.1	62.2	*h*
	64.0	105.7	83.1	77.2	82.4	62.1	*m*
	63.8	105.5	82.9	77.0	82.2	61.9	*i*
	63.8	105.5	82.9	77.0	82.2	61.9	*j*
	64.5	105.7	83.4	77.9	83.0	62.7	*k*
	63.7	105.5	82.9	77.0	82.2	61.9	*l*

TABLE I *(continued)*

Tautomeric form	*Chemical shifts in p.p.m. downfield from Me_4Si*						*Ref.*
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	
β-furanose	63.7	102.4	76.4	75.4	81.6	63.3	*a*
	63.71	102.31	76.37	75.41	81.51	63.34	*e*
	64.0	102.5	76.6	81.6	75.6	63.4	*h*
	63.8	102.8	75.6	76.6	81.8	63.4	*m*
	63.6	102.6	76.4	75.4	81.6	63.2	*i*
	63.6	102.6	76.4	75.4	81.6	63.2	*j*
	64.7	102.8	77.5	76.4	82.1	63.7	*k*
	63.6	102.6	76.4	75.4	81.6	63.2	*l*
D-Ribose							
α-pyranose	94.4	70.9	70.2	68.2	63.9	—	*a*
	94.8	70.1	71.7	69.0	64.3	—	*c*
	93.8	70.35	69.6	71.3	67.6	—	*n*
	94.65	71.15	70.35	68.4	64.1	—	*o*
β-pyranose	94.8	71.9	69.7	68.2	63.9	—	*a*
	94.9	72.1	69.5	68.4	63.9	—	*b*
	95.3	72.6	72.6	60.0	64.3	—	*c*
	95.3	70.0	72.6	72.6	64.3	—	*p*
	94.15	69.15	67.6	71.3	63.35	—	*n*
	94.95	72.15	70.1	68.35	64.1	—	*o*
α-furanose	97.2	71.9	70.9	84.0	62.3	—	*a*
	96.55	75.6	70.35 / 70.8	82.75 / 83.35	61.7	—	*n*
	97.4	72.1	71.15	84.15	62.5	—	*o*
β-furanose	101.9	76.2	71.4	83.4	63.5	—	*a*
	102.6	76.5	74.3	83.9	64.1	—	*c*
	101.25	75.6	70.35 / 70.8	83.75 / 83.35	62.9 / 62.9	—	*n*
	102.05	76.4	71.55	83.6	63.65	—	*o*

[a]Present work, in deuterium oxide, original data referenced to the highest-field resonance of DSS were converted according to the equation: $\delta Me_4Si = \delta DSS - 1.6$. [b]In water[23]. [c]In water[24]. [d]In water[14]. [e]In deuterium oxide[25]. [f]In water, chemical shifts in p.p.m. downfield from "external" Me_4Si; chemical shifts for the α- and β-furanose forms are also given in the original paper[26]. [g]In deuterium oxide[27]. [h]In water[9]. [i]In deuterium oxide[19]. [j]In water[21]. [k]In deuterium oxide[19]. [l]In deuterium oxide[20]. [m]In deuterium oxide[12]. [n]In deuterium oxide[28]. [o]In deuterium oxide[29]. [p]In water[30].

mannose, D-fructose, and D-ribose obtained in this work, together with comparative data given by other investigators. The proportions of tautomeric forms of ketoses at equilibrium in solution have been estimated from integrated and peak intensities[9], or simply from relative peak-intensities[13]. In some instances, only the resonances of anomeric carbon atoms were taken into account[12,13]. Table II shows that integrals of individual signals in the spectrum of a given tautomer may differ quite significantly from each other in ordinary, ^{13}C-n.m.r. spectra. Thus, by considering various pairs of corresponding carbon atoms (for the situation where two tautomeric forms are involved), divergent values of the composition, differing substantially from each other (see Table III), are obtained. It should also be noted at this point that the

TABLE II

INTEGRATED SIGNAL-INTENSITIES IN ^{13}C-p.F.-t., N.M.R. SPECTRA OF D-GLUCOSE, D-MANNOSE, D-FRUCTOSE, AND D-RIBOSE

Sugar	*Tautomer*	*Integrated intensities*[a] *of carbon signals*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
D-Glucose	α-pyranose	**1.00**	—	1.07	—	—	—
	β-pyranose	1.18	1.12	1.27	—	**1.00**	—
D-Mannose	α-pyranose	1.03	1.22	1.15	**1.00**	1.12	—
	β-pyranose	1.23	1.17	1.29	1.36	**1.00**	—
D-Fructose	α-pyranose	—	—	1.03	**1.00**	—	—
	β-pyranose	1.35	**1.00**	1.22	1.32	1.36	1.36
	α-furanose	—	**1.00**	1.42	1.55	1.72	—
	β-furanose	1.64	**1.00**	1.44	1.40	1.36	1.58
D-Ribose	α-pyranose	**1.00**	—	1.25	—	—	—
	β-pyranose	1.04	—	—	**1.00**	—	—
	α-furanose	**1.00**	—	—	1.04	1.30	—
	β-furanose	1.40	1.19	—	**1.00**	2.15	—

[a]The integrated intensity of the weakest line of each tautomer is set equal to unity[8]; intensities of resonances that interfere with other, closely proximal resonances are not given.

estimated compositions depend neither on the absolute difference in chemical shifts of carbon atoms considered nor on the similarity of their chemical environments. However, the data do demonstrate (for D-glucose and D-mannose as examples) that, by taking into account all peaks well separated from others, it is possible to determine compositions consistent with data obtained by other methods (see Table IV). A similar procedure has been used[16–20] in order to determine the proportions of tautomeric forms of various ketoses at equilibrium in aqueous solution; the proportions were calculated by averaging all ^{13}C signals of each form that are clearly separated from the others, except those of the anomeric carbon atoms, which, being quaternary, always give much smaller peaks than the other carbon atoms.

The present results also show that, by using this averaging procedure, the tautomeric composition determined for D-fructose from an ordinary, ^{13}C-n.m.r. spectrum is very close to that determined from ^{13}C-n.m.r. spectra recorded for a similar concentration and at the same temperature, but with a 2-s acquisition time and an 8-s delay between pulses (see Table V). For the correct quantitation of a trace component, it appears to be important to use a relatively large number of scans (up to 16,000 in the case of D-fructose; see preceding). Traces of furanose forms have been found in equilibrated, aqueous solutions of D-glucose[26] and D-mannose[34], and traces of acyclic, *keto* forms have been found in equilibrated solution of ketoses[18–20]. For the tautomeric equilibrium of D-ribose, data obtained by ^{13}C-n.m.r. spectroscopy show somewhat less accurate correlation with those obtained by ^{1}H-n.m.r. spectroscopy than do those for the other sugars examined (see Table VI).

TABLE III

EQUILIBRIUM COMPOSITIONS OF D-GLUCOSE AND D-MANNOSE IN D_2O AT $\sim 30°$ AS CALCULATED FROM PEAK AREAS OF VARIOUS CARBON SIGNALS IN ^{13}C-N.M.R. SPECTRA

Carbon atoms considered	*Absolute difference in chemical shifts* ($\delta_\alpha - \delta_\beta$)	*Content of anomers in percent*[a]	
		α-Pyranose	*β-Pyranose*
D-Glucose			
1α;1β	3.8	34	66
1α;2β	17.9	35	65
1α;3β	16.2	32.5	67.5
1α;5β	16.3	38	62
3α;1β	23.1	36	64
3α;2β	1.4	37	63
3α;3β	3.1	34	66
3α;5β	3.0	40	60
1α,3α;1β,2β,3β,5β	10.6[b]	36[b]	64[b]
D-Mannose			
1α;1β	0.4	68	32
1α;2β	22.8	69	31
1α;3β	21.0	67	33
1α;4β	27.4	66	34
1α;5β	18.0	72	28
2α;2β	0.6	72.5	27.5
2α;3β	2.4	70.5	29.5
2α;4β	4.0	69	31
2α;5β	5.4	75.5	24.5
3α;1β	23.4	70	30
3α;2β	1.0	71	29
3α;3β	2.8	69	31
3α;4β	3.6	68	32
3α;5β	5.8	74	26
4α;1β	26.8	67	33
4α;2β	4.4	68	32
4α;3β	6.2	66	34
4α;4β	0.2	65	35
4α;5β	9.2	72	28
5α;1β	21.3	70	30
5α;2β	1.1	71	29
5α;3β	0.7	69	31
5α;4β	5.7	67.5	32.5
5α;5β	3.7	74	26
1α,2α,3α,4α,5α;1β,2β,3β,4β,5β	9.6[b]	70[b]	30[b]

[a] ±2%. [b] Averaged values for the group of signals considered.

TABLE IV

COMPARISON OF ANOMERIC EQUILIBRIA DETERMINED FOR D-GLUCOSE AND D-MANNOSE BY VARIOUS METHODS

Tautomeric form	*Content of α and β anomers (in percent)*					
	Rotation[a]	*Bromine oxidation*[a]	*G.l.c.*[b]	*^{1}H-N.m.r.*[c]	*^{13}C-N.m.r.*	*^{13}C-N.m.r.*
D-Glucose						
α-pyranose	36.2	37.4	38.2	38	36[d]	37.3[e]
β-pyranose	63.8	62.6	61.8	62	64[d]	62.6[e]
D-Mannose						
α-pyranose	68.8	68.9	68.4	65.5	70[f]	63[g]
β-pyranose	31.2	31.1	31.6	34.5	30[f]	36[g]

[a]In water at 0° (ref. 31). [b]In 3M HCl at 100° (ref. 32). [c]In D_2O at ~31° (ref. 33). [d]Present work; 1.5M solution in D_2O at ~30°; 2100 scans, 8192 data points, spectral width 5.000 kHz, pulse repetition-time 1 s; percentages (±2%) were obtained from the arithmetical averages of the integrated intensities of the resonances of carbon atoms 1, 2, 3, and 5 of the anomers. [e]Solutions (0.2–2.8M) in water at 42°, 4,096–18,0224 accumulations, 16,384 data points, spectral width 3.788 kHz, pulse repetition-time 2.1 or 1.1 s; percentages (±1%) were obtained from the arithmetical averages of the integrated intensities of the resonances of carbon atoms 1, 2, 3, and 5 of each of the anomers; 0.14 ±0.02% of the β-*f* tautomer were also found at equilibrium[26]. [f]Present work, 1.5M solution in D_2O at ~30°; 2048 scans, 8192 data points, spectral width 5.000 kHz, pulse repetition-time 1 s; percentages (±2%) were obtained from the arithmetical averages of the integrated intensities of the resonances of carbon atoms 1–5 of each of the anomers. [g]Solutions (4M) in water at 36°; 16,384 accumulations, 16,384 data points, spectral width 5.000 kHz, pulse repetition-time 1.03 s; percentages (±1%) were obtained from the arithmetical averages of the integrated intensities of the resonances of carbon atoms 1–5 of each of the anomers; 0.6 ±0.1% of the α-*f* and 0.3 ±0.1% of the β-*f* tautomer were also found at equilibrium[34].

The foregoing procedure, using ordinary, partially relaxed, ^{13}C, p.F.-t., n.m.r. spectra, provides, for the four sugars studied, tautomeric compositions of an accuracy comparable with those obtained by more-sophisticated, magnetic-resonance procedures. The results allow confidence to be placed in the use of similar procedures for determining the equilibrium compositions of D-glucaric acid and its lactones[36], and those of D-aldonic acids and their lactones[37] in aqueous solution, as described in the accompanying papers.

TABLE V

TAUTOMERIC EQUILIBRIUM OF D-FRUCTOSE BY ^{13}C-N.M.R. SPECTROSCOPY

Content of tautomeric forms in percent[a]				*Ref.*
α-Pyranose	*β-Pyranose*	*α-Furanose*	*β-Furanose*	
2	70	5	23	*b*
3 (±1)	57 (±6)	9 (±1)	31 (±3)	*c*
<5	60	10	30	*d*
0	72	5	23	*e*
traces	75	4	21	*f*
2.65	64.8	6.5	25.25	*g*

[a]The (acyclic) *keto* form has also been found by ^{13}C-n.m.r. spectroscopy: 2 ±1% in pyridine-d_5 at 33° (ref. 18); 3% in D_2O at 80° (ref. 19); and 0.80% in D_2O at 31° (ref. 20). [b]Present work; solutions (1.5M) in D_2O; the compositions (±2%) are based on areas of all of the peaks of protonated carbon atoms well separated from others; 16,000 scans, 16,384 data points, repetition time 1 s, spectral width 4.000 kHz. [c]In water at 36°; the composition was obtained by measurement of integrated peaks and peak intensities[9]. [d]In water; ±2–3%, the composition was calculated from relative peak-intensities of the signals of the anomeric carbon atoms in the ^{13}C-n.m.r. spectrum, and from integration of the anomeric OH signals in the ^{1}H-n.m.r. spectrum[10,13]. [e]Solutions (1–2M) in deuterium oxide at 30°; ±2%, the compositions were based on peak areas of anomeric carbon atoms; 4580 scans, 8192 data points, 2-s acquisition time, 8-s delay[12]. [f]Solutions (1.5–2M) in D_2O; the composition (±5%) was obtained by averaging all signals of each form clearly separated from others, except those of the anomeric carbon atoms; 30,000–100,000 scans, 8192 data points, repetition time 1.1 s, spectral width 3.750 kHz (ref. 17). [g]Solutions (4M) in D_2O at 31°; ±5%, 20,000–80,000 scans, repetition time[20] 1.4–2.2 s.

TABLE VI

TAUTOMERIC EQUILIBRIUM OF D-RIBOSE BY N.M.R. SPECTROSCOPY

Content of tautomeric forms in percent				*Ref.*
α-Pyranose	*β-Pyranose*	*α-Furanose*	*β-Furanose*	
19	64	6	11	*a*
18	54	12	16	*b*
21.5	58.5	6.5	13.5	*c*
20.3	62	6.1	11.6	*d*

[a]Present work, solutions (1.8M) in D_2O at ~30°, by ^{13}C-n.m.r. spectroscopy; 2200 scans, 8192 data points, spectral width 5.000 kHz, pulse repetition-time 1 s; percentages (±2%) were obtained from the arithmetical averages of the integrated intensities of resonances of C-1 and C-3 of the *α-p* form, C-1 and C-4 of the *β-p* form, C-1, C-4, and C-5 of the *α-f* form, and C-1, 2, 4, and 5 of the *β-f* form. [b]In D_2O at 70°, by ^{1}H-n.m.r. spectroscopy[35]. [c]In D_2O at 31°, by ^{1}H-n.m.r. spectroscopy[33]. [d]Solutions (M) in D_2O at 30°, by ^{13}C-n.m.r. spectroscopy; 5000 scans, 16,384 data points, spectral width 3.000 kHz, pulse repetition-time 5.7 s; percentages were obtained from the intensities of the C-1 resonances of each of the tautomers[29].

REFERENCES

1 D. HORTON AND Z. WAŁASZEK, *Abstr. Pap. Am. Chem. Soc. Meet.*, 170 (1975) CARB-10.
2 G. C. LEVY AND G. L. NELSON, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley–Interscience, New York, 1972; J. B. STOTHERS, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972.
3 G. N. LA MAR, *J. Am. Chem. Soc.*, 93 (1971) 1040–1041.
4 G. C. LEVY AND V. EDLUND, *J. Am. Chem. Soc.*, 97 (1975) 4482–4485.
5 R. FREEMAN, H. D. W. HILL, AND R. KAPTEIN, *J. Magn. Reson.*, 7 (1972) 327–329.
6 L. CATTEL, J. F. GROVE, AND D. F. SHAW, *J. Chem. Soc., Perkin Trans. 1*, (1973) 2626–2629.
7 J. N. SHOOLERY AND W. C. JANKOWSKI, *Varian Application Note NMR-73-4*, Pub. No. MAG-724.
8 A. ALLERHAND, D. DODDRELL, AND R. KOMOROSKI, *J. Chem. Phys.*, 55 (1971) 189–198.
9 D. DODDRELL AND A. ALLERHAND, *J. Am. Chem. Soc.*, 93 (1971) 2779–2781.
10 A. S. PERLIN, P. C. M. HERVE DU PENHOAT, AND H. S. ISBELL, in *Carbohydrates in Solution, Adv. Chem. Ser.*, 117 (1973) 39–50.
11 T. A. W. KOERNER, JR., L. N. CARY, N. S. BHACCA, AND E. S. YOUNATHAN, *Biochem. Biophys. Res. Commun.*, 51 (1973) 543–550.
12 L. QUE, JR., AND G. R. GRAY, *Biochemistry*, 13 (1974) 146–153.
13 P. C. M. HERVE DU PENHOAT AND A. S. PERLIN, *Carbohydr. Res.*, 36 (1974) 111–120.
14 G. DE WIT, A. P. G. KIEBOOM, AND H. VAN BEKHUM, *Tetrahedron Lett.*, (1975) 3933–3946.
15 J. W. BLUNT AND M. H. G. MUNRO, *Aust. J. Chem.*, 29 (1976) 975–986.
16 S. J. ANGYAL, G. S. BETHEL, D. E. COWLEY, AND V. A. PICKLES, *Aust. J. Chem.*, 29 (1976) 1239–1247.
17 S. J. ANGYAL AND G. S. BETHEL, *Aust. J. Chem.*, 29 (1976) 1249–1265.
18 W. FUNCKE AND A. KLEMER, *Carbohydr. Res.*, 50 (1976) 9–13.
19 W. FUNCKE, C. VON SONNTAG, AND C. TRIANPHYLIDES, *Carbohydr. Res.*, 75 (1979) 305–309.
20 G. J. WOLFF AND E. BREITMAIER, *Chem. Ztg.*, 103 (1979) 232–233.
21 T. A. W. KOERNER, JR., R. J. VOLL, L. N. CARY, AND E. S. YOUNATHAN, *Biochem. Biophys. Res. Commun.*, 82 (1978) 1273–1278.
22 R. CHERNIAK, R. G. JONES, AND D. S. GUPTA, *Carbohydr. Res.*, 75 (1979) 39–79.
23 D. W. DORMAN AND J. D. ROBERTS, *J. Am. Chem. Soc.*, 92 (1970) 1355–1361.
24 A. S. PERLIN, B. CASU, AND H. J. KOCH, *Can. J. Chem.*, 48 (1970) 2596–2605.
25 P. E. PFEFFER, K. M. VALENTINE, AND F. W. PARRISH, *J. Am. Chem. Soc.*, 101 (1979) 1265–1274.
26 C. WILLIAMS AND A. ALLERHAND, *Carbohydr. Res.*, 56 (1977) 173–179.
27 P. A. J. GORIN AND M. MAZUREK, *Can. J. Chem.*, 53 (1975) 1212–1223.
28 E. BREITMAIER, G. JUNG, AND W. VOELTER, *Chimia*, 26 (1972) 136–139.
29 E. BREITMAIER AND U. HOLLSTEIN, *Org. Magn. Reson.*, 8 (1976) 573–575.
30 A. S. PERLIN, N. CYR, H. KOCH, AND B. KORSCH, *Ann. N. Y. Acad. Sci.*, 222 (1973) 935–942.
31 H. S. ISBELL AND W. W. PIGMAN, *J. Res. Natl. Bur. Stand.*, 18 (1937) 141–194.
32 T. GHEORGHIU AND K. OETTE, *J. Chromatogr.*, 48 (1970) 430–445.
33 S. J. ANGYAL AND V. A. PICKLES, *Aust. J. Chem.*, 25 (1972) 1695–1710.
34 D. J. WILBUR, C. WILLIAMS, AND A. ALLERHAND, *J. Am. Chem. Soc.*, 99 (1977) 5450–5452.
35 M. RUDRUM AND D. F. SHAW, *J. Chem. Soc.*, (1965) 52–57.
36 D. HORTON AND Z. WAŁASZEK, *Carbohydr. Res.*, 105 (1982) 95–109.
37 D. HORTON AND Z. WAŁASZEK, *Carbohydr. Res.*, 105 (1982) 111–129.