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F.T.-I.R. AND LASER-RAMAN SPECTRA OF D-RIBOSE AND 2-DEOXY-D-*erythro*-PENTOSE ("2-DEOXY-D-RIBOSE")*

MOHAMMED MATHLOUTHI, ANNE MARIE SEUVRE,

Département "Biologie Appliquée", Institut Universitaire de Technologie, Université de Dijon, B.P. 510-21014 Dijon-Cédex (France)

AND JACK L. KOENIG

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106 (U.S.A.)

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ABSTRACT

Laser-Raman spectra of D-ribose and 2-deoxy-D-*erythro*-pentose in aqueous solution are reported. F.t.-i.r. and Raman spectra have been obtained for crystals of these sugars. Assignments of the Raman bands observed in solution are proposed. The spectral differences between the two sugars are discussed in terms of the structural difference. The analysis of the frequencies observed permits identification of each of the sugars and their isomeric analogs, and can be used as a basis for study of nucleosides and nucleotides by vibrational spectroscopy.

INTRODUCTION

Vibrational-spectroscopic methods have been used in the study of biological molecules and, especially, of the nucleic acids. The general strategy in the spectroscopic study of polymers consists in investigating the modes of vibration of monomers and model molecules as a basis for analysis of the spectra of related macromolecules, but this approach does not seem to be the rule for study of nucleosides and nucleotides. Most of the publications in this area have dealt directly with DNA, RNA, or polynucleotides. The initial aim was to acquire, by using spectroscopic techniques, an understanding of the general conformation and function of the macromolecules, or of the differentiation of the forms (*i.e.*, A, B, and Z for DNA) obtained in various chemical environments.

It had been established[1] that the handedness of nucleic acids has its origin in the pseudorotation of the furanose constituent. However, although the importance of the conformations of D-ribose (**1**) and 2-deoxy-D-*erythro*-pentose (**2**) had been noted in previous work[2,3] on nucleosides and nucleotides, no spectroscopic study

*F.t.-i.r. and Laser-Raman Spectra of Constituents of Nucleic Acids, Part I.

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has been undertaken on pure **1** and **2** in either the solid form or in solution. The spectra of these sugars were analyzed, among those of other carbohydrates, in studies of complexation[4] of boric acid with sugars, and of the low-frequency vibrations of nucleosides[5].

When the vibrations of **1** or **2** have been evoked in the nucleic acid literature, the assignments of the vibrations observed have not been given in detail. The structural complexity of these molecules, and their lack of symmetry, render the assignment of all of the frequencies observed an almost insurmountable task, but, as was suggested[6] for assignment of the vibrations of D-glucose and sucrose, it is less important to know the contribution, to a Raman line, of each of the various modes of vibration as given by normal, coordinate analysis than to assign the most prominent vibration to that line. Such assignments, based on comparative study of different carbohydrates, and the complementary information given by i.r. and Raman spectra, should allow the monitoring, by their shifts in frequencies and intensities, of modifications of the structures by the environment. Change in the environment may result from the insertion of D-ribose (**1**) or 2-deoxy-D-*erythro*-pentose (**2**) in the structure of nucleotides and nucleosides, or from the effect of such physical factors as the temperature and interactions with solvents.

We now suggest interpretations of the Raman spectra of aqueous solutions of **1** and **2**, and compare the F.t.-i.r. and laser-Raman spectra of their crystalline forms, in order to propose the most probable assignments of the intense lines to certain structural vibrations. The assignments proposed may then be used as reference marks in the future study of nucleosides and nucleotides.

EXPERIMENTAL

Aqueous solutions of D-ribose (**1**) and 2-deoxy-D-*erythro*-pentose (Sigma) (**2**) were respectively prepared by dissolving each in distilled water. The concentration of the analyzed solutions, obtained by direct weighing, were 22% (w/w) for **1**, and 20% for **2**. The solutions were filtered through a membrane, and placed in sample tubes (2 mm i.d.).

The samples were placed in a Spex sample-chamber, and the scattered flux was focused on the slits of a Spex 1400 double monochromator, at right angles to the beam. Spectra were recorded by using the 514.5-nm laser line of a Spectra Physics model 165 laser. To illuminate the solutions, 500 mW of power was used, and 350 mW for the solid samples. The slit width was 4 cm^{-1}.

I.r. spectra were recorded with a Digilab Fourier-transform, infrared spectrometer (FTS 20).

RESULTS AND DISCUSSION

A. Aqueous solutions

General aspects of the spectra. — The Raman spectra of solutions of **1** and **2**

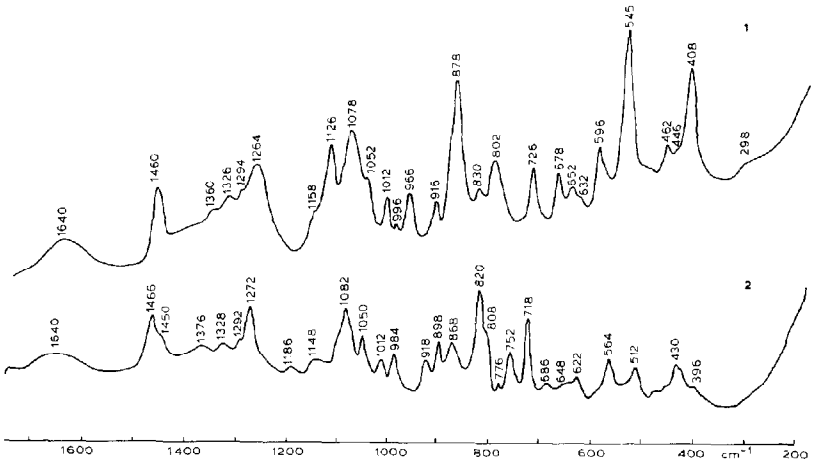
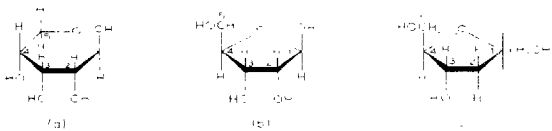


Fig. 1. Laser-Raman spectra of aqueous solutions of D-ribose (**1**) and 2-deoxy-D-*erythro*-pentose (**2**).

are shown in Fig. 1. In the region below 1700 cm^{-1}, the spectral background of solutions of **1** show two intensity-maxima (besides the sharper vibrations), namely, one at ~1640 cm^{-1}, which is distinct, and another (more diffuse) between 800 and 300 cm^{-1}. The 1640-cm^{-1} maximum, observed in the spectra of solutions of both **1** and **2**, is due to H_2O, whereas the broad band (800–300 cm^{-1}) is observed only in the spectrum of **1**, as a background. This large band probably corresponds to the scattering associated with the libration movement[7] of H_2O.

The absence of such a band is noted in the spectra of solutions of D-fructose. This feature characterizes the solute–solvent interactions in aqueous solutions of D-fructose, which are different from those of D-glucose and sucrose. The difference of background observed in Fig. 1 probably has its origin in the molecular interaction with water. The differences in interactions with water, as well as the differences in the structure of **1** and **2** are revealed by their intrinsic viscosities and heats of dilution[8].

Although molecules of D-ribose and 2-deoxy-D-*erythro*-pentose differ only at the level of the substituents on C-2 (see Scheme 1), features of their spectra show important differences. Between 1500 and 1200 cm^{-1}, the CH_2 vibrations (1460 for **1**) are split in two (1450, 1466) in the spectrum of **2**. One of the sharpest lines (876 cm^{-1}) of the spectrum of **1** is absent from the spectrum of **2**, but there are 2 lines, at 898 and 868 cm^{-1}. This region is generally specified as the anomeric region[9], as it is the region characteristic for the anomers of D-glucose[10,11]. The skeleton region shows important modifications of intensities and frequencies when Fig. 1 is studied in the range of frequencies up to 600 cm^{-1}.



Scheme 1. Numbering of atoms in (a) β-D-ribopyranose, (b) 1,2-O-ribofuranose and (c) 2-deoxy-β-D-erythro-pentofuranose

The differences observed could be due to the presence, in the ring of **2**, of a methylene group having a strong, hydrophobic effect[12]. Such a CH_2 group is also present in β-D-fructopyranose[13].

Analysis of the observed bands. — a. The 1700–1200-cm⁻¹ region. The absence of peaks at 1720–1700 cm⁻¹ indicates the absence of carbonyl groups of the acyclic forms (which are intermediate forms in the pyranose–furanose equilibrium).

The only vibration present as a strong line is situated at 1640 cm⁻¹, and is assigned to $\delta(H_2O)$. Molecules of neither **1** nor **2** have any symmetry elements. The oscillator strength depends on the local symmetry conditions. All of the vibrations between 1500 and 1200 cm⁻¹ are depolarized. They have their origin in the only symmetrical group in the carbohydrates, namely, the CH_2 group (C_5). In the spectrum of **1**, the vibration at 1460 cm⁻¹ could be assigned to the CH bending-mode. In the spectrum of **2**, this vibration is split in two (one line at 1466, and a shoulder at 1450 cm⁻¹). The CH_2 group, having the carbon atom strongly held in the ring, requires more energy to vibrate, and this results in a mode at 1466 cm⁻¹. The vibration at 1450 cm⁻¹ could be assigned to the $\delta(CH_2)$ mode of the hydroxymethyl group. Comparison of the bending frequencies of CH_2 in the hydroxymethyl groups of **1** and **2** shows a shift of 10 cm⁻¹ towards the higher frequencies for the former; this shift could arise from the interactions with water, because, owing to its endocyclic CH_2, **2** is more hydrophobic than **1**, and this hydrophobic hydration lessens the direct hydrogen-bonding of water with sugar **2**. The CH_2OH group of **1** is more hydrophilic and is engaged in hydrogen bonding, and this constraint yields a higher energy of the CH_2 bending mode in the CH_2OH group. The higher hydrophobic character of **2** is also shown by viscosimetric and thermodynamic results[8].

The vibrations at 1326 cm⁻¹ (for **1**) and 1328 cm⁻¹ (for **2**) could be assigned to the wagging of CH_2 in the hydroxymethyl group. The 1376-cm⁻¹ band (of **2**) could have its origin in the wagging of C-2-H_2. A shoulder is observed at 1360 cm⁻¹ (for **1**) which arises from the wagging of CH_2. The relatively intense lines at 1264 cm⁻¹ (for **1**) and 1272 cm⁻¹ (for **2**), which are depolarized, may be assigned to the twisting of CH_2 in C-5-H_2OH. The wagging and twisting modes of CH_2 in the 1360–1150-cm⁻¹ region had been suggested by different authors[14–16].

The vibrations at 1292 cm^{-1} (for **2**) and 1294 cm^{-1} (for **1**), which are present as shoulders in the spectra, could be assigned to the twisting of CH_2 in different environments. Indeed, the aqueous solution of each of the sugars is composed of different isomers which have their specific interactions with water. As shown for D-glucose, the CH_2 vibrations are shifted when the environment (concentration, isomeric proportions) is varied[17].

b. The 1200–700-cm^{-1} region. This region was identified by Tul'chinsky *et al.*[9] as the anomeric region sensitive to structure. Most of the vibrations found in this range of frequencies are due primarily to the deformation of the CCH and COH angles. The most characteristic vibrations are those involving C-1, the anomeric center of the molecule. Besides the anomeric equilibrium $\alpha \rightleftharpoons \beta$, there is a pyranose $\rightleftharpoons$ furanose equilibrium which influences the vibrations in this region and that of the skeleton region below 600 cm^{-1}. All of these features contribute to the difficulty in making specific assignments of the frequencies observed between 1200 and 700 cm^{-1}. However, advantage may be taken of the results of comparison of the two spectra, and previous results on other sugars[6,13] may be utilized in order to propose assignments.

As a general rule, the endocyclic vibrations of furanoses are more energetic than the equivalent vibrations of the pyranoses. This observation originates from the fact that the furanoid ring is more compact than the pyranoid. By adopting this rule, we found[13] proportions of fructofuranoses and fructopyranoses which were in good agreement with those found by other techniques. In the 1200–1000 cm^{-1} region, the frequencies of C–O stretching and COH bending modes are found. Thus, the 1158- and 1126-cm^{-1} bands could be assigned to the C–O stretching in the D-ribo-furanoses and -pyranoses, respectively. The vibrations at 1186 and 1148 cm^{-1} observed in the spectrum of solutions of **2** should correspond to the C–O stretching mode in the furanose and pyranose forms. Lord and Thomas[18] localized the C–O vibration in the D-ribosyl group of uridine and cytidine at 1125 and 1080 cm^{-1}, and Peticolas[19] assigned the 1049-cm^{-1} band to the C–O stretching in yeast RNA. The COH bending mode could occur at 1078 and 1052 cm^{-1} for the pyranoid and furanoid forms of D-ribose, respectively.

All of the COH angles of the pyranose involve a carbon atom of the ring, whereas an exocyclic CH_2OH group exists in the furanose. The deformation of a COH totally out of the ring would cause it to vibrate at a lower frequency. In the spectrum of **2**, the COH vibrations are located at approximately the same frequencies as for **1**, namely, 1082 and 1050 cm^{-1}. The C–H deformations, and especially the C–H of C-1 are at the origin of the zone of anomeric frequencies (1000–800 cm^{-1}). Different kinds of C–H bending vibrations may be observed: exocyclic O–C–H and C–C–H (belonging to the CH_2OH group), endocyclic O–C–H (O-4–C-1–H and O-4–C-4–H, see Scheme 1), and endocyclic C–C–H (having their carbon atoms in the ring). As a general rule, endocyclic vibrations occur at higher frequencies than exocyclic. These conclusions led us to propose the assignments of the CH deformations shown in Table I (D-ribose) and Table II (2-deoxy-D-*erythro*-pentose).

TABLE 1

BANDS OBSERVED[a] IN LASER-RAMAN AND F.T.-I.R. SPECTRA OF D-RIBOSE

Solid samples				*Aqueous solutions*				
I.r.		*Raman*		ν(cm^{-1})	*I*	ρ	*Assignments (modes)*	*Structure*
ν(cm^{-1})	*I*	μ(cm^{-1})	*I*					
		170	8.6					
		190	2.9					
		204	2.9					
		218	4.8					
		242	3.8					
		288	12.4					
				298	6.1	P	δ(O-H · · · O)	
		318	13.3					
		363	20.0					
		396	12.4					
		408	13.3	408	70.9	P	δ(C–O–C)	*p*
		424	48.6					
		444	18.1	446	26.5	P		
		466	12.4	462	29.6	P	δ(C–O–C)	*f*
		490	7.6					
		516	6.2					
		546	100[b]	545	100[b]	P	δ(C–C–C)	*p*
				596	35.7	P	δ(C–C–C)	*f*
		602	24.8					
628	37.4	634	30.5	632	6.2			
655	27.6	658	11.4	652	16.3	P	δ(O-4–C-1–O-1) β	
				678	27.6	P	δ(O-4–C-1–O-1) α	
725	30.3	730	13.3	726	28.1	P	δ(C–C–O) exo	
750	22.0							
804	16.5	808	13.3	802	37.8		δ(C–C–O) endo	*p*
				830	22.4		δ(C–C–O) endo	*f*
866	22.8							
		876	20.0	878	86.7	P	ν(C–C)	*p*
890	27.2	890	58.6					
910	33.5	914	24.8	916	20.4	P	ν(C–C)	*f*
922	31.5							
950	55.5	936	40.0					
957	57.5	946	13.3					
				966	26.5	D	δ(C–C–H)	
		992	13.3	996	10.2	D	δ(C–C–H)	
		1006	20.0					
1016	66.1	1018	15.2	1012	27.0	D	δ(O–C–H)	
1035	100[b]	1032	24.8					
		1052	33.3	1052	38.8	D	δ(C–O–H)	*p*
		1060	56.2					
1076	52.0	1076	44.8	1078	64.3	P	δ(C–O–H)	*f*
1086	56.3							
		1092	29.5					

TABLE I *(continued)*

Solid samples				*Aqueous solutions*				
I.r		*Raman*		$\nu(cm^{-1})$	*I*	ρ	*Assignments (modes)*	*Structure*
$\nu(cm^{-1})$	*I*	$\mu(cm^{-1})$	*I*					
1116	62.6							
		1122	43.8	1126	57.1	P	ν (C–O)	*p*
1135	51.2	1134	20.0					
1150	51.2	1152	21.0					
1160	68.5	1164	21.9	1158	23.5	D	ν (C–O)	*f*
1175	43.3							
1220	20.9	1224	9.5					
		1236	13.3					
1245	29.5	1248	18.1					
				1264	52.0	D	τ (C-5–H_5)	
		1274	41.9					
1280	44.1	1282	28.6					
				1294	49.0	D	τ (CH_2)	
1315	29.1							
1320	28.3	1322	31.4	1326	35.0	D	ω (CH_2)	
1340	32.6							
1365	33.9	1362	23.8	1360	30.0	D	ω (CH_2)	
1380	35.4							
		1404	17.1					
1415	29.9							
		1434	12.4					
1440	37.0							
1455	31.5	1456	26.7	1460	45.0	D	δ (CH_2)	
		1466	19.0					
1635	4.3			1640	17.9	D	δ (H_2O)	

[a]Key: exo = exocyclic; endo = endocyclic; *f* = furanose; *p* = pyranose; α = α anomer, β = β anomer; I = relative intensity; D = depolarized; P = polarized; δ = bending mode; ω = wagging; τ = twisting; and ν = stretching mode. [b]Taken as reference.

One of the highest tensor elements (that corresponds to the most stable valence bond) is that of C–C. This tensor element is an essential part of the valence vibrations of the ring. We could assign the 878-cm^{-1} band, one of the most intense lines in the D-ribose spectrum, to the ν(C–C) mode in the pyranose ring (4 endocyclic C–C bonds), whereas the 916-cm^{-1} band could correspond to ν(C–C) in the furanose. In the spectrum of **2**, the C–C stretching-mode should correspond to the strong line at 820 cm^{-1}, and the shoulder at 808 cm^{-1}, to the endocyclic and exocyclic (C-4 and C-5) vibrations, respectively (see Fig. 1). The assignment of the C–C vibrations of the molecular skeleton in the region of 900–800 cm^{-1} is comparable to that proposed for D-glucose[6] and D-fructose[13], and to the results obtained with polymers[14,15].

The vibrations observed at 830 and 802 cm^{-1} in the spectrum of a solution of D-ribose could be assigned to the endocyclic C–C–O vibrations in the furanose and

TABLE II

BANDS OBSERVED[a] IN LASER-RAMAN AND F.T.I.R. SPECTRA OF 2-DEOXY-D-*erythro*-PENTOSE

Solid samples				*Aqueous solutions*				
I.r.		*Raman*		ν(cm^{-1})	*I*	ρ	*Assignments (modes)*	*Structure*
ν(cm^{-1})	*I*	μ(cm^{-1})	*I*					
		160	6.0					
		184	3.4	186		P		
		216	2.3					
		252	11.7					
		280	3.8					
		302	2.6					
		332	6.0					
		382	20.0					
		392	13.6	396	20.5	P	δ(C–O–C)	
		420	18.8					
				430	38.5	P	δ(C–O–C)	
		440	8.3					
		472	4.2					
		482	4.9					
		508	3.4	512	32.5	P	δ(C–C–C)	*t*
		530	9.0					
		544	19.6					
		560	7.5	564	40.2	P	δ(C–C–C)	*p*
				622	23.9	P	δ(O–C–O) β	
633	42.9	630	16.2					
				648	18.8	P	δ(O–C–O) α	
672	19.7							
686	13.4	680	16.2	686	13.7	P	δ(C-4–C-5–O-5)	
				718	73.5	P	δ(C–C–O) endo	
740	18.1							
		756	13.6	752	43.6	P	δ(C–C–O) exo	
760	50.4							
		766	10.2					
770	42.5							
				776	11.1			
815	51.2	812	100[b]	808	53.8	P	ν(C–C) exo	
		842	2.3	820	100[b]	P	ν(C–C) endo	
		862	2.3	868	49.6	P		
880	17.3	880	13.2					
896	71.3	904	10.2	898	46.2	P	δ(C–C–H) exo	
				918	29.1	P	δ(C–C–H)	
926	12.6	926	18.9					
		948	4.2					
985	92.1	980	8.7	984	31.6	P	δ(O–C–H) exo	
		990	8.7					
				1012	23.9	P	δ(O-4–C-1–H)	
1017	100[b]	1020	18.1					
1045	51.6	1044	20.8					
		1052	15.1	1050	44.4	D	δ(C–O–H)	*p*
		1078	10.2	1082	67.5	D	δ(C–O–H)	*t*
1092	65.0	1088	16.6					
1116	95.7	1120	13.2					

TABLE II (*continued*)

Solid samples				*Aqueous solutions*				
I.r.		*Raman*		$\nu(cm^{-1})$	*I*	ρ	*Assignments (modes)*	*Structure*
$\nu(cm^{-1})$	*I*	$\mu(cm^{-1})$	*I*					
1152	33.9	1152	12.8	1148	15.4	D	ν (C–O)	*p*
		1168	3 4					
				1186	6.8	D	ν (C–O)	*f*
1200	61.4	1200	4.9					
1236	29.5	1240	7.2					
1260	48.8	1264	6 0					
		1276	10 6	1272	61.5	D	τ (C-5–H_2)	
1280	22.0	1284	14 0					
				1292	32.5		τ (CH_2)	
1303	20.5	1302	15.1					
		1324	2 3	1328	29.1	D	ω (CH_2)	
1344	50.4							
1350	48.0	1354	12.5					
1370	18.9							
				1376	29.1	D	ω (C-2–H_2)	
		1382	6.0					
1390	42 1	1394	4.9					
1415	36.2	1420	3.0					
1440	37.8	1444	5.7					
				1450	46.2	D	δ (C-5–H_2)	
				1466	51.3	D	δ (C-2–H_2)	
1470	34.6	1474	33.2					
1635	7.1			1640	18.8	D	δ (H_2O)	

[a]Key: exo = exocyclic; endo = endocyclic; *f* = furanose; *p* = pyranose; α = α anomer; β = β anomer; I = relative intensity; D = depolarized; P = polarized; δ = bending mode, ω = wagging; τ = twisting; and ν = stretching mode. [b]Taken as reference.

pyranose, respectively. The ratios of intensities I(830):I(802), I(916):I(876), and I(1052):I(1078) are comparable, and approximately equal to 1:4, and this supports our assignment to furanoid and pyranoid forms, respectively. Indeed, the solutions of D-ribose (**1**) at equilibrium are composed of 76% of pyranoses and 24% of furanoses[20].

The endocyclic and exocyclic, C–C–O vibrations of **2** should correspond to the frequencies 752 and 718 cm^{-1}, respectively. The differences in intensity are probably due to the number of C–C–O angles (2 endocyclic and 3 exocyclic). The C–C–O angles of the CH_2OH group, which has all of its atoms outside the ring, need less energy to vibrate, and their vibrations could take place at 726 cm^{-1} for D-ribose and at 686 cm^{-1} for **2**.

c. The region of frequencies below 700 cm^{-1}. The vibrations in this region are characteristic of the ring. The hemiacetal character of both sugars is revealed by O-4–C-1–O-1 deformation, which occurs at 678 cm^{-1} for the β and at 652 cm^{-1} for the

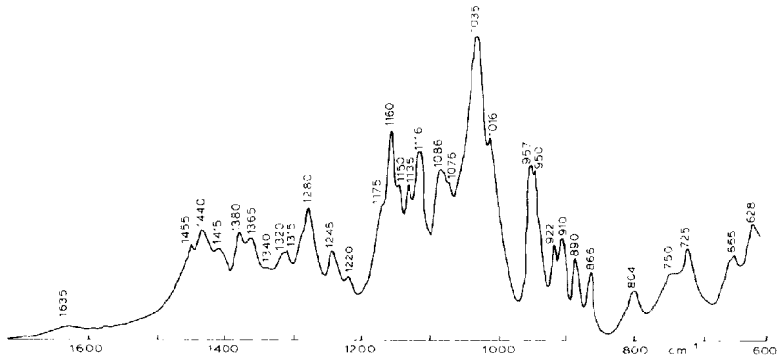


Fig. 2. F.t.-i.r. spectrum of solid D-ribose (**1**)

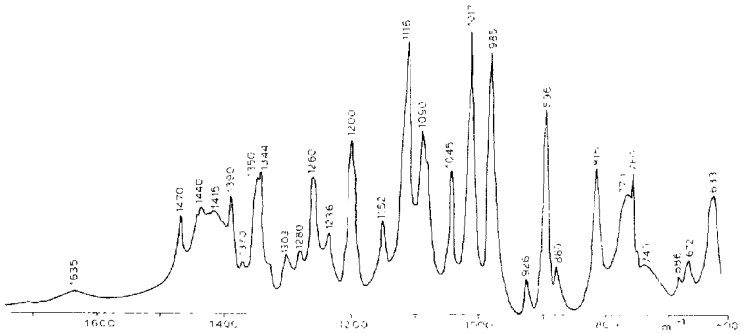


Fig. 3. F.t.-i.r. spectrum of solid 2-deoxy-D-*erythro*-pentose (**2**)

α anomer of D-ribose. In the spectrum of **2**, these vibrations probably correspond to the lines at 648 and 622 cm^{-1}. The antisymmetrical property of this vibration is revealed by an intense line in the i.r. spectrum of D-ribose at 628 cm^{-1} (see Fig. 2), and at 633 cm^{-1} for **2** (see Fig. 3). The frequencies at 596 and 548 cm^{-1} observed in the spectrum of a solution of **1** could be assigned to furanoid and pyranoid C–C–C bending, respectively, whereas the bands at 462 and 408 cm^{-1} should correspond to the C–O–C vibrations. The vibrations corresponding to the furanoses have almost one quarter of the intensity of those assigned to the pyranoses; this is in good agreement with the proportions found by n.m.r.-spectral techniques[21]. In the spectrum of aqueous solutions of **2**, the frequencies at 564 and 512 cm^{-1} are assigned

to C–C–C bending modes, and at 430 cm^{-1} to C–O–C (see Table II). The shoulder observed at 298 cm^{-1} in the spectrum of solutions of **1** is probably due to the hydrogen bonding caused by the aqueous environment. As already mentioned, D-ribose seems to be more sensitive to the interactions with water than is 2-deoxy-D-*erythro*-pentose.

B. Solid samples

Comparison of the i.r. and the Raman spectra below 1700 cm^{-1}. — *a.* D-*Ribose* (**1**). The vibrations observed in the 1500–600-cm^{-1} region recorded by the i.r. and Raman techniques show important differences in their frequencies and intensities. In the local symmetry region between 1500 and 1200 cm^{-1}, the relative intensities of the i.r. (see Fig. 2) and Raman (see Fig. 4) bands are comparable. The out-of-plane deformation (wagging) of CH_2, at 1380 and 1365 cm^{-1}, are more intense in the i.r. spectrum. The twisting modes of CH_2 at 1280 (i.r.) and 1274 cm^{-1} (Raman) have the same relative intensities in both spectra. The region (1200–800 cm^{-1}) specified as the anomeric region shows more-important differences in the spectra. In this range of wavelengths, we find deformations of the angles, including atoms in and out of the ring, which make them nonsymmetrical. This feature could explain the very strong intensity of the 1035-cm^{-1} vibration in the i.r. spectrum, which is assigned to C–O–H bending.

The C–O stretching vibrations, localized at 1160–1116 (i.r.) and 1164–1122 cm^{-1} (Raman) are more intense in the i.r. spectrum. Indeed, there is a lack of homogeneity in the length, and the position (C–O–C or C–O–H), of these valence bonds, as seen from the values given by Arnott and Hukins[2], namely, C-4–O-4 (en-

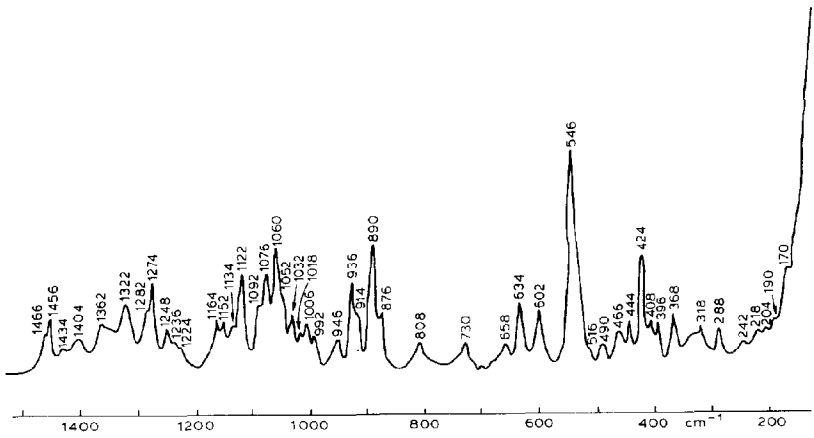


Fig. 4. Laser-Raman spectrum of solid D-ribose (**1**)

docyclic) = 145.7 ±2, C-1–O-4 (endocyclic) = 141.9 ±2.3, C-2–O-2 (exocyclic) = 141.7 ±1.9, and C-3–O-3 (exocyclic) = 142.2 ±2.1 pm.

Between 1000 and 900 cm^{-1}, the CCH deformations are found. As these deformations take place out of the plane, and are influenced by the puckering of the furanoid ring[22], they contribute to an important change of the dipole moment, and hence, to a strong infrared absorption. Consequently, the C–C–H bending modes could be localized at 957–950 cm^{-1} in the i.r. spectrum of D-ribose (see Fig. 2). The Raman intensity of δ(C–C–H) at 946 cm^{-1} is relatively weak. The C–C stretching generally occurs in the 900–800-cm^{-1} region. As mentioned for the aqueous solution, the furanose-ring vibrations are more energetic. We observed a very sharp peak at 890 cm^{-1} in the Raman spectrum (see Fig. 4) which could be assigned to C–C stretching in β-D-ribofuranose. The intensity of this vibration is very weak in the i.r. spectrum (see Fig. 2).

Below 800 cm^{-1}, the skeletal vibrations are observed. Their intensities are relatively weak in both the i.r. and the Raman spectra. The frequencies at 750 and 725 cm^{-1} (see Fig. 2) could be assigned to the C–C–O bending, and at 655–628 cm^{-1}, to δ(O–C–O). The last vibration, which occurs around C-1, a center of chirality in the molecule, is more intense in the i.r. than it is in the Raman spectrum (see Fig. 4).

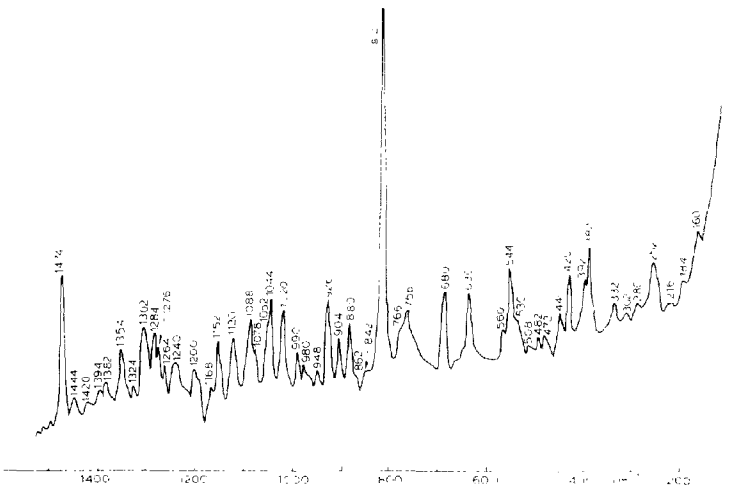


Fig. 5. Laser-Raman spectrum of solid 2-deoxy-D-*erythro*-pentose (2)

Only the Raman spectrum of solid **1** is recorded below 600 cm^{-1}. As in the case of the aqueous solution (see Fig. 1), the sharpest line is found at 546 cm^{-1}; this could have its origin in the bending of the C–C–C grouping. Many weak vibrations observed in this region could be assigned to the crystal-lattice modes.

b. 2-Deoxy-D-erythro-*pentose* (**2**). The bands observed in the i.r. and Raman spectra of solid **2** are shown in Figs. 3 and 5, respectively. The general aspect of these spectra is different from that of those of D-ribose (see Figs. 2 and 4). Although the structural differences between the two sugars are weak (see Scheme 1), the environment of each of the vibrations is modified, and changes are seen as regards the frequencies and the intensities.

Whereas the i.r. and Raman intensities of the CH_2 vibrations are comparable for D-ribose (**1**), this does not seem to apply for the spectra of **2**. The vibration at 1474 cm^{-1}, which is assigned to the bending of C-2–H_2, is very sharp in the Raman spectrum (see Fig. 5). Indeed, the CH_2 group rigidly held by C-2 (see Scheme 1) is not perturbed by the electronegativity of an oxygen atom, as is the CH_2 belonging to a hydroxymethyl group. The out-of-plane deformations of CH_2 result in a more intense infrared absorption in the region 1440–1200 cm^{-1} (see Fig. 3). It is especially important to note that the frequency 1200 cm^{-1}, which could be assigned to the twisting of CH_2, may be used to characterize compound **2**.

The absence of O-2 in **2** (see Scheme 1) provokes important changes in the anomeric region (1200–800 cm^{-1}) compared to the observed spectra of D-ribose. The overlapping of the CCH and COH vibrations is not seen. Most of the lines are well resolved, and the selection rule applies clearly to the i.r. vibrations, which are more intense than the equivalent Raman bands. We could assign the i.r. bands observed at 1152 and 1116 cm^{-1} to the C–O stretching modes, at 1090 and 1045 cm^{-1} to C–O–H bending, and at 1017 cm^{-1} to O–C–H deformation. The 985-cm^{-1} line is absent from the i.r. spectrum of **1** (see Fig. 2). It could be assigned to CCH bending around C-2. Comparison of the spectra of **1** and **2** in the anomeric region should be useful from an analytical point of view when it is desired to differentiate between the two sugars. The 900–800-cm^{-1} region contains other C–H deformations and the C–C stretching vibrations. The very sharp line in the Raman spectrum at 812 cm^{-1} (see Fig. 5) could be assigned to ν(C–C). The C–C stretching in the ring is not affected by electronegativity of the oxygen substituent on C-2 that is present in D-ribose, and this enhances the symmetry and the Raman intensity of the C–C valence vibration.

The C–C–O bending modes could occur at 770–760 cm^{-1} (i.r.) and 766–756 cm^{-1} (Raman). Their intensities are relatively strong, owing to the important number of C–C–O angles. The vibrations at 633 cm^{-1} (i.r.) and 630 cm^{-1} (Raman) may be assigned to δ(O–C–O), as in the spectra of D-ribose.

Below 600 cm^{-1}, the Raman spectrum of **2** (see Fig. 5) shows differences in the relative height of the peaks, compared to those of D-ribose (see Fig. 4). The skeleton vibrations (CCC and COC) are also affected by the change in the substituent on C-2. All of the differences in the i.r. and Raman spectra of D-ribose and

2-deoxy-D-*erythro*-pentose could be used as reference marks in differentiating between their nucleosides and nucleotides.

Region of frequencies 3600–2600 cm^{-1}. — *a.* D-*Ribose* (**1**). This region of frequencies is characteristic of C–H and O–H stretching. It is apparent from Figs. 6 (i.r.) and 7 (Raman) that the relative intensities of i.r. absorption and Raman scattering are different. The valence vibration of the hydrogen atom attached to the

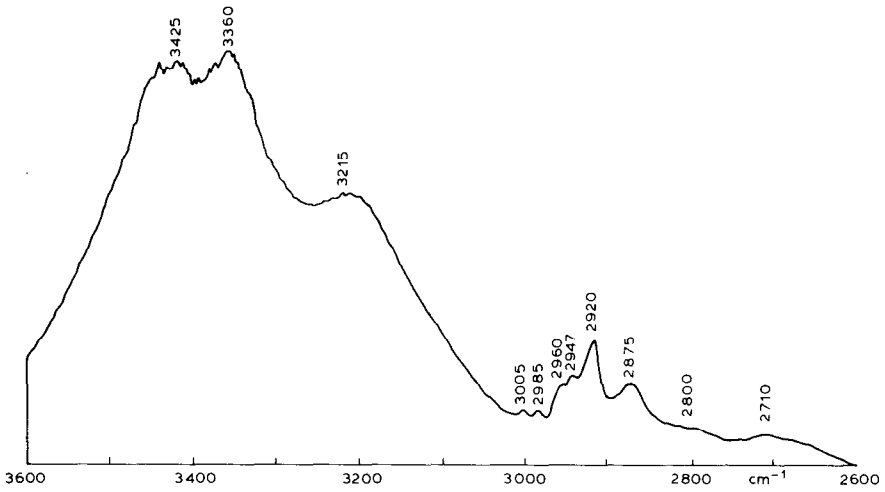


Fig. 6. F.t.-i.r. spectrum of solid D-ribose (**1**) in the region of frequencies 3600–2600 cm^{-1}.

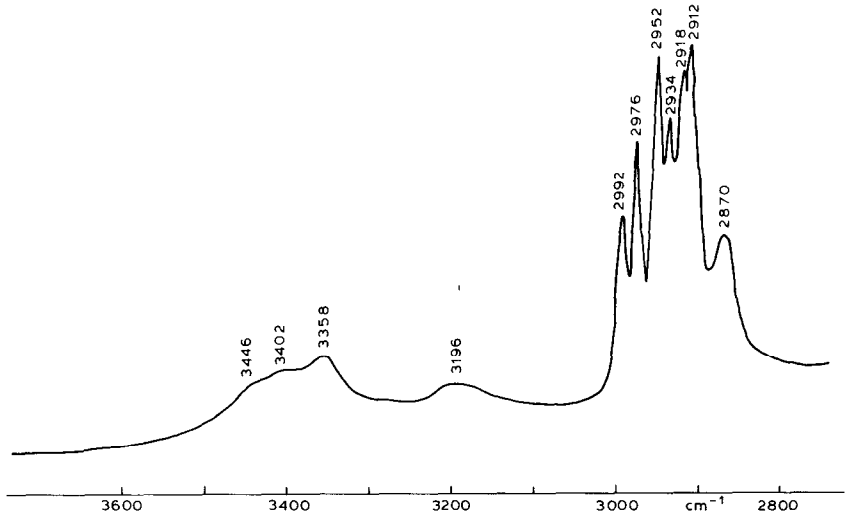


Fig. 7. Laser-Raman spectrum of solid D-ribose (**1**) in the region of frequencies 3600–2800 cm^{-1}.

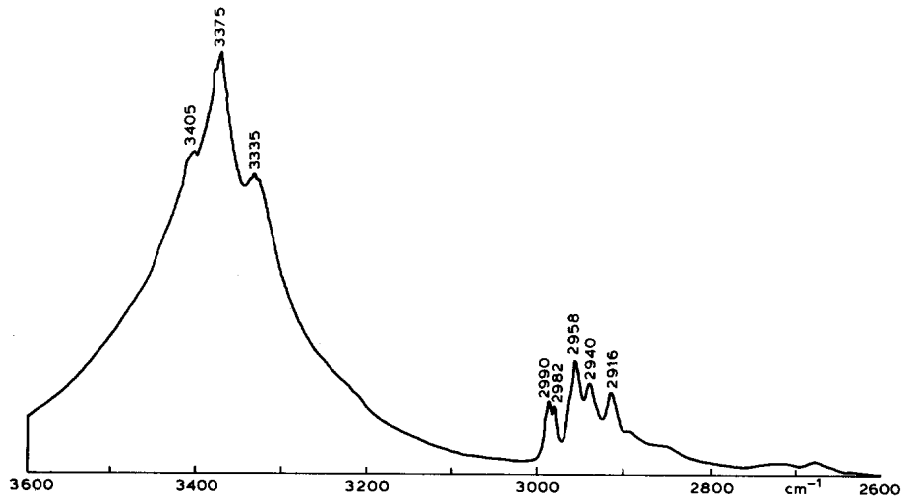


Fig. 8. F.t.-i.r. spectrum of solid 2-deoxy-D-*erythro*-pentose (**2**) in the region of frequencies 3600–2600 cm^{-1}.

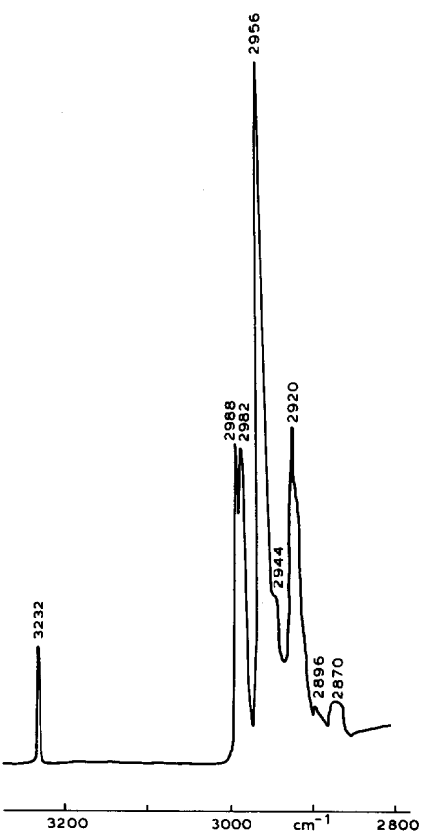


Fig. 9. Laser-Raman spectrum of solid 2-deoxy-D-*erythro*-pentose (**2**) in the region of frequencies 3600–2800 cm^{-1}.

anomeric carbon atom could take place near 2800 and 2710 cm^{-1} in the i.r. spectrum, as in those of aldehydes[23]. The CH_2 group in the CH_2OH group gives rise to two characteristic bands at 2875 (i.r.) and 2870 cm^{-1} (Raman), and 2920 (i.r.) and 2912 cm^{-1} (Raman), probably corresponding to the in-phase and out-of-phase vibrations of the hydrogen atom. The doubling of 2912 cm^{-1} (Raman) could be due to a Fermi resonance between ν(C–H) and the first overtone of $\delta(CH_2)$. The presence of oxygen atoms in the vicinity of other C–H bonds contributes to an enhancement of the frequencies.

As concerns the OH vibrations, they are broad in both the i.r. and the Raman spectra because of the hydrogen bonding. Around 3200 cm^{-1} (3215 in the i.r. and 3196 in the Raman) are found the OH vibrations engaged in the hydrogen bonding of the crystal. The secondary alcohol groups probably give rise to the 3360-cm^{-1} i.r. vibration (see Fig. 6) and the 3358-cm^{-1} Raman band (see Fig. 7). The frequencies 3425 cm^{-1} (i.r.) and 3402 cm^{-1} (Raman) could be assigned to the OH stretching of the primary alcohol group. All of the OH-vibration frequencies are shifted towards the lower values because of the intermolecular H bonding.

b. 2-Deoxy-D-erythro-*pentose* (**2**). The i.r. and Raman spectra of **2** in the region of frequencies above 2700 cm^{-1} are shown in Figs. 8 and 9, respectively. The differences observed in the intensities and frequencies of the Raman CH vibrations, compared to those of D-ribose (see Fig. 7) are due to the CH_2 group attached to the ring. The OH region is also different from that of D-ribose. The OH infrared absorption is narrower, showing less hydrogen bonding. The OH stretching is not shown in the Raman spectrum (see Fig. 9), as it is very weak; only one line at 3232 cm^{-1} is observed.

CONCLUSION

The analysis of the Raman and i.r. spectra of the sugars present in nucleic acids has led us to propose assignments for the bands observed. The structural differences between the sugars primarily entail the substituent on C-2, but the spectra recorded show frequency shifts, and variations of relative intensities, in the whole range of frequencies. The changes are enhanced in aqueous solution, because the differences in structure between D-ribose and 2-deoxy-D-*erythro*-pentose influence their interactions with the environment. The modifications of frequencies and intensities observed are localized in the regions sensitive to the CH_2 vibrations, namely, the local, symmetrical region for the CH_2 bending, the anomeric region for the out-of-plane CH deformation, and the CH-stretching range of frequencies. Some of the differences observed could be used in analytical differentiation of the two sugars. The characteristic bands of **1** and **2**, even after the change of environment resulting when they are present in nucleic acids, should be recognizable by comparison to the spectra of the pure compounds.

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