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The Infrared Spectra of Some Carbohydrates

by

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In connection with our studies on cellulose and related substances [1] we have been interested in some aspects of the infrared spectra of carbohydrates, particularly in the position of the bands due to water of crystallization and those due to the cyclic (pyran) structures.

A series of nine sugars including mono-, di-, and trisaccharides were examined. Their purity was tested by means of the specific rotation and melting point measurements. A full list of the substances and their physical characteristics are given in Table I. Some of the sugars were examined both as hydrated and as anhydrous forms.

TABLE I

No.	Sugar	Melting point °C	$(\alpha)^{20}_{D}$ (H_2O) after 24 h
1.	L(+)-arabinose	158–9	+105°
2.	D(+)-xylose	144–6	+ 18.2°
3.	L(−)-sorbose	157–160	− 44.0°
4.	D(−)-ribose	85–7	+ 19.9°
5.	D(+)-glucose	147–9	+ 52.5°
6.	D(+)-mannose	130–2	+ 14.5°
7.	lactose	250–2 hydrate 202–3	+ 53.0°
8.	sucrose	180–185 hydrate 165–170	+ 66.5°
9.	raffinose hydrate ($5H_2O$)	78–79	+106°

A Hilger H-800 double-beam recording spectrometer with a 60° NaCl prism was used. The samples were ground with Nujol (ratio 50:50), and then placed between NaCl plates to form thin films. The spectra were measured within the range of 4000–750 cm^{-1}. They are given in Figs. 1–9. The broken lines represent the range of strong absorption by Nujol; the dotted ones show the bands assigned to water of crystallization.

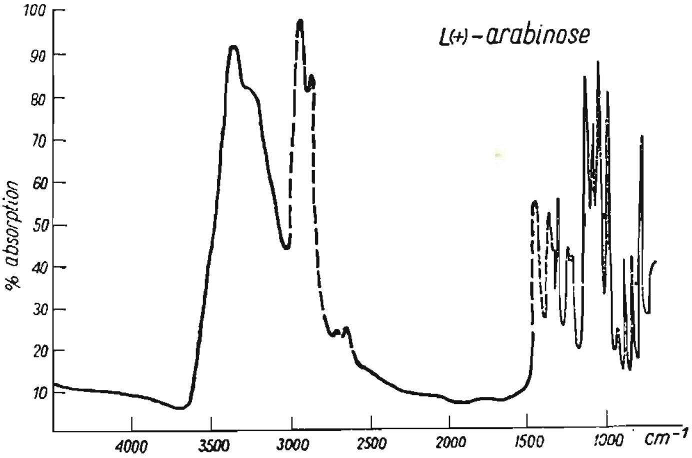

Fig. 1

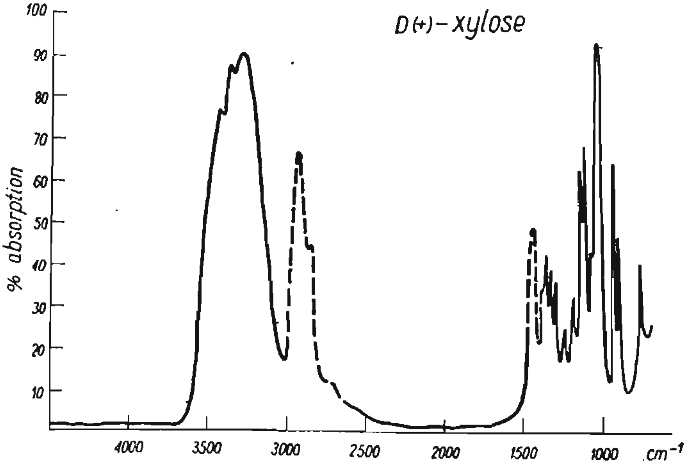

Fig. 2

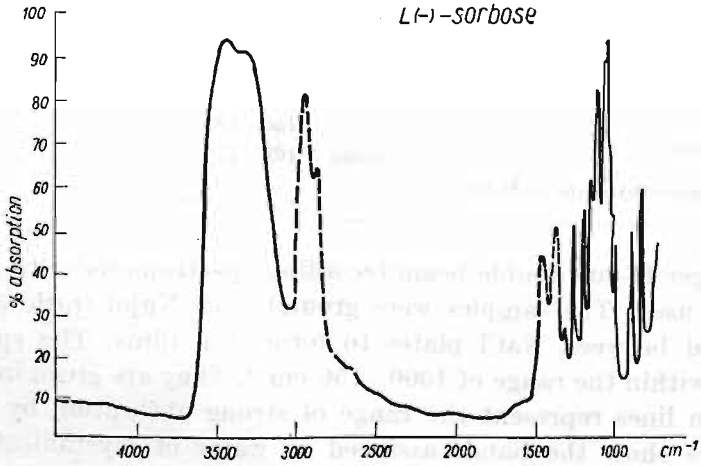

Fig. 3

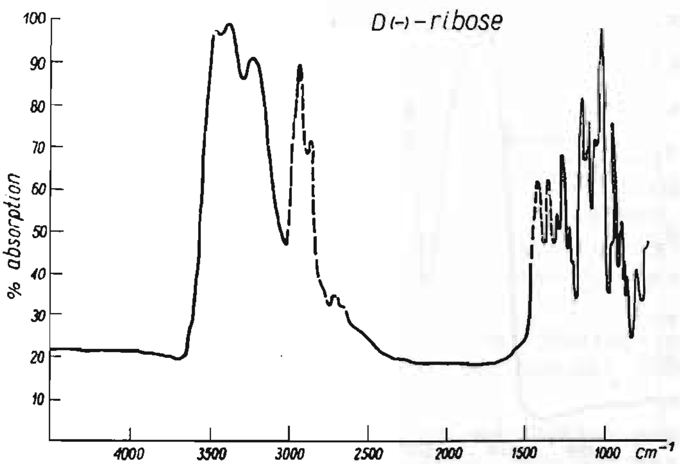

Fig 4

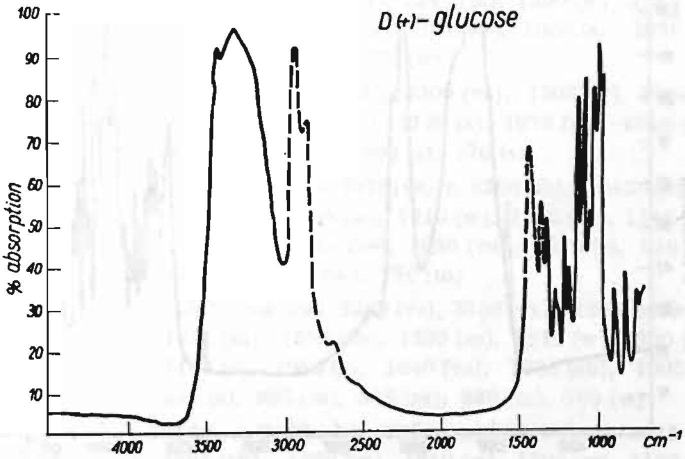

Fig. 5

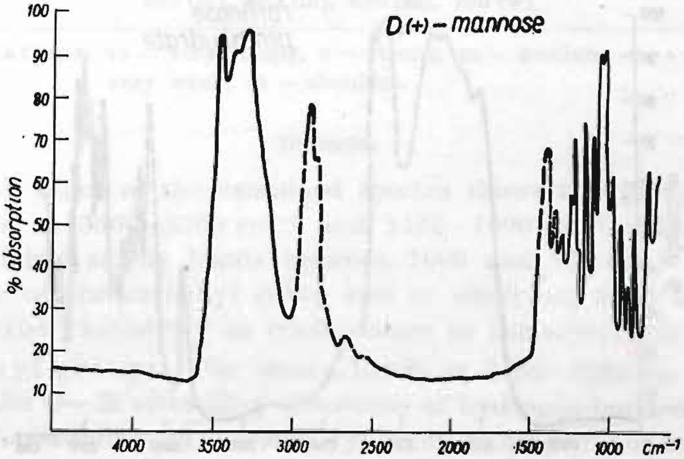

Fig. 6

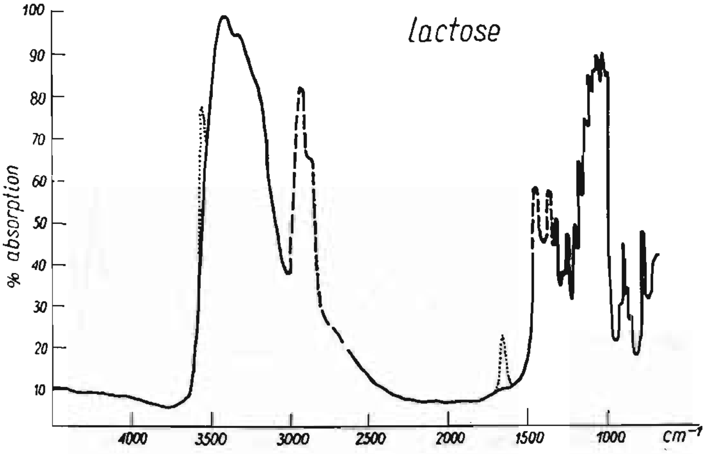

Fig. 7

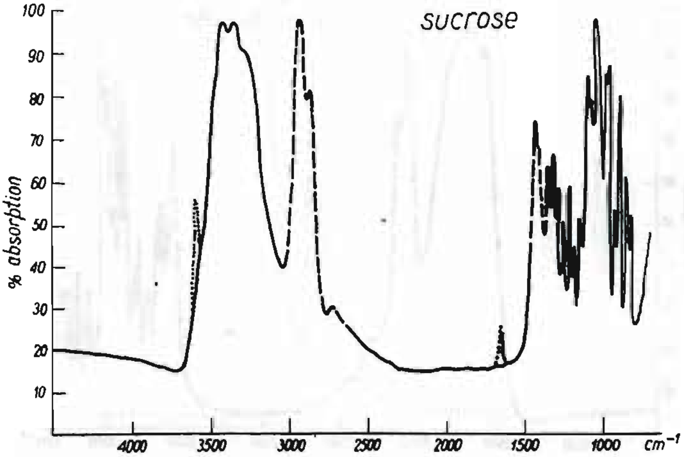

Fig. 8

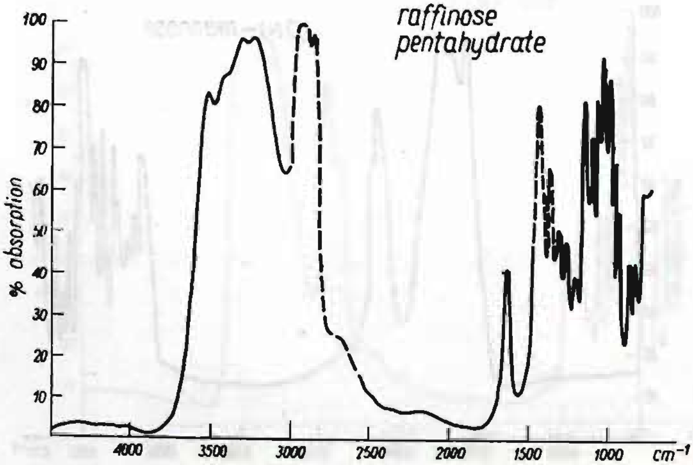

Fig. 9

The frequencies can be found in Table II.

TABLE II

No.	Sugar	Band frequencies cm⁻¹
1.	L(+)-arabinose	3330 (vs), c. 3250 (sh), 1315 (w), 1255 (m), 1230 (m), 1130 (s), 1095 (vs), 1055 (vs), 1005 (s), 945 (w), 895 (m), 845 (m), 785 (s)
2.	D(+)-xylose	3420 (sh), 3340 (vs), 3250 (vs), 1335 (m), 1305) m), 1240 (w), 1190 (w), 1155 (s), 1130 (s), 1080 (sh), 1040 (vs), 1030 (sh), 940 (vs), 910 (s), 760 (s)
3.	L(−)-sorbose	3400 (vs), c. 3300 (sh), 1305 (w), 1260 (s), 1195 (s), 1150 (m), 110 (vs), 1080 (sh), 1050 (vs), 1025 (sh), 1000 (m), 900 (sh), 880 (s), 830 (s)
4.	D(−)-ribose	3420 (vs), 3370 (vs), 3210 (vs), 1315 (w), 1280 (m), 1240 (w), 1220 (sh), 1165 (s), 1135 (sh), 1120 (m), 1065 (w), 1040 (vs), 950 (s), 915 (sh), 905 (m), 890 (w), 870 (w), 805 (w)
5.	D(+)-glucose	3430 (vs), 3320 (vs), 1340 (m), 1300 (w), 1230 (m), 1205 (w), 1150 (vs), 1115 (vs), 1080 (w), 1050 (s), 1030 (vs), 1005 (s), 920 (m), 840 (s), 770 (w)
6.	D(+)-mannose	3450 (vs), 3350 (sh), 3300 (vs), 1305 (w), 1260 (w), 1235 (s), 1215 (vw), 1175 (s), 1120 (s), 1070 (vs), 1045 (vs), 1015 (m), 940 (s), 900 (m), 860 (s), 770 (s)
7.	lactose	(3560-hydrate), 3370 (vs), c. 3300 (sh), (1645-hydrate), 1235(w), 1280 (sh), 1250 (w), 1210 (w), 1185 (m), 1145 (w), 1120 (vs), 1090 (vs), 1065 (vs), 1030 (vs), 1010 (s), 910 (sh), 890 (m), 875 (w), 855 (vw), 770 (m)
8.	sucrose	(3580-hydrate), 3380 (vs), 3350 (vs), (1645-hydrate), 1350 (m), 1325 (m), 1305 (sh), 1260 (m), 1210 (w), 1200 (w), 1150 (vs), 1105 (s), 1080 (s), 1040 (vs), 1035 (sh), 1000 (vs), 970 (s), 940 (s), 895 (m), 885 (m), 830 (m), 760 (w)
9.	raffinose pentahydrate	3560, c. 3400 (sh), 3330 (vs), 3200 (vs), 1645 (s), 1320 (m), 1305 (sh), 1260 (m), 1210 (w), 1200 (w), 1150 (vs), 1105 (s), 1080 (s), 1045 (vs), 1035 (sh), 1000 (vs), 970 (s), 940 (s), 895 (m), 885 (m), 830 (m), 760 (w)

Abbreviations: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder.

Discussion

General. Each of the examined spectra shows two groups of very strong bands at 3500–3200 cm⁻¹ and 1150–1000 cm⁻¹. There is also a group of fairly strong bands between 1000 and 750 cm⁻¹ No bands characteristic of the carbonyl group can be observed, so it seems that the sugars exist exclusively as cyclic forms in the crystalline state.

Hydroxyl groups. The strong bands at 3500–3200 cm⁻¹ may be assigned to the O—H stretching vibrations of hydrogen-bonded hydroxyl groups. The possibility of various types of hydrogen bonds accounts for the differences in the over-all shape of absorption in this range.

At least one of the bands between 1085 and 1050 cm^{-1} [2] should be assigned to the C—OH stretching vibration (the range is given for an alicyclic secondary alcohol having a 5- or 6-membered ring, as well as for a primary saturated alcohol). In the infrared spectra of alkyl and alicyclic alcohols it is the strongest band between 1350 and 750 cm^{-1} [3]. Therefore, the band involved is probably that near 1050 cm^{-1}, which is very strong in each case.

Cyclic structures. Since no bands corresponding to the carbonyl group are observed, the sugars are supposed to exist only as cyclic forms in the crystalline state. These forms contain acetal, hemi-acetal or ketal structures, which should be detectable in the spectra. Bergmann and Pinchas [4] note strong bands at 1190–1158, 1143–1124, 1098–1063 and 1056–1038 cm^{-1} for some simple ketals and acetals. The spectra of the sugars exhibit strong bands at 1190–1150, 1130–1120, and near 1110, 1080, 1050, 1030 and 1005 cm^{-1}. These may be attributed to the acetal and ketal structures of the sugars except the band at c. 1050 cm^{-1}, which is probably due to the C—OH stretching vibration (see above).

The strong bands at 990 and 970 cm^{-1} in the spectra of lactose and raffinose, respectively, have no corresponding bands in the spectra of the other sugars. Since only these two of the sugars contain —O—C—O—C—O— structures, the bands quoted might be due to some coupled vibration of this system.

The bands between 950 and 750 cm^{-1} are characteristic of the α- and β-anomers of the cyclic forms [5]. As the sugars had been crystallized from water, both the anomers were probably present in the samples, so no assignments could be made.

Water of crystallization. Two sharp bands are observed in the spectra of the sugar hydrates. One lies between 3580 and 3540 cm^{-1}; the other at 1645 cm^{-1}. These bands disappear after the hydrate has been kept for several hours in an oven at a temperature close to its melting point and then in a dessicator. Therefore, the two bands should be assigned to the O—H stretching and O—H deformation vibrations respectively of the water bound in the hydrated crystals.

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