Infrared Absorption Spectra in the Study of Mutarotational Equilibria of Monosaccharides

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The infrared absorption spectra (in the range of 5000 to 250 cm⁻¹) of 6 anomeric pairs of sugars and of 12 single anomers are presented, together with the spectra (in the range of 5000 to 667 cm⁻¹) of the dry lyophilizates of the respective equilibrium solutions of these 18 sugars in water.

Analysis of the spectra indicated the presence, in a number (possibly, in all) of the equilibrium mixtures, of some of the carbonyl form (aldehydo or keto) of the respective sugar. Conclusions as to the other components of each equilibrium mixture agreed with those derived from mutarotational studies, except for p-lyxose and p-ribose. Despite the reported absence of mutarotation for *b-gluco*-heptulose and *p-manno*-heptulose, the equilibrium mixture of each was found to contain one or more forms different from that originally dissolved.

1. Purpose and Scope of the Project

This project was primarily undertaken with the objective of gaining, for a number of monosaccharides, information regarding the composition of the sugar mixture obtained by dissolving one anomer of a sugar in water and allowing the solution to reach mutarotational equilibrium. Each such solution was freed from water by lyophilization; and the infrared absorption spectrum of the product was recorded and then compared with the spectrum of the crystalline anomer originally dissolved (and with that of the other anomer, if available).

The second objective was to record these spectra for use in (a) the identification of monosaccharides and (b) eventual assignment of conformation to each crystalline anomer. For 6 sugars, the infrared spectrum, in the range of 5000 to 667 cm⁻¹, was recorded for *both* crystalline anomers and for the equilibrium mixture. For 12 other sugars, only *one* crystalline anomer was available; its infrared spectrum and that of the corresponding equilibrium mixture were recorded in the above range. The infrared spectra in the range of 667 to 250 cm⁻¹ were also recorded for the crystalline anomers.

2. Sugars Investigated

Table 1 gives a list of the sugars, their code numbers [1],¹ and an index to the spectrograms; the serial number of a sugar is the same as the number of its spectrogram, and the letter E is appended to designate an equilibrium mixture. The 24 anomers were classified into 4 groups; the members of each group have like configurational features.

2.1. Sugars of the xylo Configuration

The members of this group have the general formula I, if they are pyranoid.



- 1. α -D-Xylose, R=H; R'=OH; and R''=H.
- 2. (?)-L-xylo-Hexulose (L-sorbose), R = OH and $R' = CH_2OH$, or vice versa; R'' = H; and the molecule is the mirror image of that depicted.
- 5. α -D-Glucose, $\mathbf{R} = \mathbf{H}$; $\mathbf{R}' = \mathbf{OH}$; and $\mathbf{R}'' = \mathbf{CH}_2\mathbf{OH}$.
- 6. β -D-Glucose, R=OH; R'=H; and R''=CH₂OH.
- 7. $\alpha(i)$ -n-gluco-Heptulose, $R = CH_2OH$; R' = OH; and $R'' = CH_2OH$.

2.2. Sugars of the lyzo Configuration

These sugars, if pyranoid, have the general formula II.



 $^{^1}$ Figures in brackets indicate the literature references at the end of this paper. The references for tables 1 and 2 are given at the ends of the tables.

- 8. α -p-Lyxose, R=H: R'=OH: and R'' and R''' ______T
- 9. β -D-Lyxose, R=OH; and R', R'', and R''=H.
- 10. (?)-n-lyzo-Hexulose (D-tagatose), R=CH.OH and R'=OH, or vice versa; and R'' and R'''=Ħ.
- 11. 6-Deoxy- α -L-mannose (α -L-rhamnose) monohydrate, R=H: R'=OH: R''=H: R'''=CH: and the molecule is the mirror image of that depicted.
- 12. 6-Deoxy-β-L-mannose (β-L-rhamnose), R=OH; R'=H; R''=H; R'''=CH₃; and the molecule is the mirror image of that depicted.
- 13. α -D-Mannose, R=H; R'=OH; R''=H; and R''' $=CH_{2}OH_{1}$
- 14. β -p-Mannose, R=OH; R'=H; R''=H; and R''' $=CH_{2}OH.$

TABLE 1. Compounds measured and index to spectrograms.

Code	Sugar	Retarences	Spectro- gram
10.1170. 10.1100. 10.7170. 10.7100. 10.21708999	exp-Xylate. b-Xylate (quilibrium). (?)-t.tylo-Hexulate (equilibrium). c-p-Glucose 0.5 NaCl-0.5 HgO	1, 2 3, 4	1 1-E 2-E 3
10.217099. 10.2110 b. 10.2100(99] 10.2170. 10.8170. 10.8100.	a-D-Glucese, monohydrata a-D-Glucese D-Glucese (quillbrium) a-D-Glucese (quillbrium) a(7)-D-gluce-Heptulose D-gluce-Heptulose (quillbrium)	6,7 2,6 to ¥ 2,7,10 11	4 0,6∽E 6 7 7−E
10.12?0 10.1200 10.12?0 10.72?0 10.72?0 10.7200	a-o-Lyxose (equilibrium), p-Lyxose (equilibrium), p-Lyxose (7)-o-igro-Hexulose (equilibrium), p-lyro-Hexulose (equilibrium),	2, 12 to 14 2, 14 15	8,9-K 9,9-K 10 10-K
10.2270(5)8099 10.2200(5)8099 10.2270(5)80 10.2270(5)80 10.2270 10.22909	6-Deoxy-o-L-mannose, monohydrate 4. 6-Deoxy-a-mannose (oquilibrium) 6-Deoxy-8-L-mannose. 	2.16 	11, 13–E 12 13 13, 14–E
10.22?0 10.82?0 10.8200 10.26709669 10.26009899	\$-p-Manno40. (?)-p-manno-Heptulose. n-manno-Heptulose (equilibrium) (?)-p-Guluse 0.5 CaCh-0.5 HyO. p-Guluse 0.6 CaCh (equilibrium)	9.21 22 2	14 15 15-E 16 16-E
10.1370 10.1300 10.73709999	 P-Arabinose D-Arabinose (equilibrium) (?) D-arabino-Heaulose *0.5 CaCly1.5 BeO. 	23 24	17 17-E 18
10.73009899	p-arabino-Herulose 0.5 CaCl, (equi- librium). 2.6 Methyl-(?)-n-arabino-hexulase	25	18-E
10.7800(3)11	8-0-Methyl-D-orobino-besulose (equi-		19-R
10.8210(3)7699	#Drum), \$-p-maane-3-Heptulose, monohy- drate. ^t	25	20
10.8200(3)7090 10.2370(6)80 10.2300(6)80	p-manno-3-Heptulase (equilibrium) ¹ 6-Deory-a-t-galactose f 6-Deory-6-galactose (equilibrium)	27 to 30	20–E 21 21–E
10.2370 10.2300 10.2370 10.8776899	a-D-Oalactose p-Gulactose G-O-Galactose 2,7-Anhydro-g-D-sitro-heptalose, ^b menebulante	2, 31 to 34 2, 81 to 34 35	22 22,23-E 23 24
10.8700+ 10.8776899, etc.)	Mixture from acid treatment of com- pound 24 (equilibrium)		24-B
10.14?0 10.1400 10.2470 10.2470 10.2470	β(T)-p-Ribose p-Ribose (equilibrium)	36, 37 2, 38, 39 39	25 25-E 26 25,27-E 27

• Trivial name: Leorbose, b c-D-Glucopyrances has the CA conformation [T. B. B. McDonald and C. A. Beevers, Acta Cryst. 3, 654 (1952)]. • Trivial name: D-tagatose. 4 Trivial name: c-t-ripances monohydrate. • Trivial name: p-dructose, • (Kindly presented by R. Schaffer. • Trivial name: c-t-fucese. • Trivial name: sedobeptulesan. • See taxt, sec. 6.2.

- 15. (?)-D-manno-Heptulose, R=CH₂OH and R' =OH, or vice versa; R''=H; and R''' $=CH_{2}OH_{1}$
- 16. (?)-D-Gulose 0.5 CaCl, 0.5 H.O. R=H and R' =OH, or vice versa; R"=CH₂OH; R"=H; and the molecule is the mirror image of that denicted.

2.3. Sugars of the arabino Configuration

These sugars, if pyranoid, have the general formula IT.



- 17. β-D-Arabinoso, R=OH: R'=H; and R" and R" **≕**Η.
- 18. (?)-D-arabino-Hexulose (D-fructose) 0.5 CaCl₂ 1.5 H₂O, R=OH and R'=CH₂OH, or vice versa: and $\mathbf{R}^{\prime\prime}$ and $\mathbf{R}^{\prime\prime\prime} = \mathbf{H}$.
- 19. 3-O-Methyl-(?)-p-arabino-hexulose, R=OH and $R' = CH_*OH$, or vice versa: $R'' = CH_*$; and $\mathbf{k}''' = \mathbf{H}$
- **20.** β -p-manno-3-Heptulose monohydrate. R=OH:

$$R'=HOH_2C-C$$
; and R'' and $R'''=H$.

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- 21. 6-Deoxy- α -L-galactose (α -L-fucose), R = OH; R' = H; R'' = H; and $R''' = CH_3$. 22. α -D-Galactose, R = OH; R' = H; R'' = H; R''' = H; R'''
- 22. a-D-Galactose, R=OH; R'=H; R''=H; R'' =CH₂OH; and the molecule is the mirror image of that depicted.
- 23. β-D-Galactose, R=H, R'=OH; R''=H; R''' =CH₂OH; and the molecule is the mirror image of that depicted.

Compound 24 (sedoheptulosan) has the following formula (IV).



24. 2.7-Anhydro-8-D-altro-heptulopyranose

2.4. Sugars of the ribo Configuration

The pyranoid forms of these sugars have the general formula V.



- **25.** β -n-Ribose, R=OH; R'=H; and R''=H.
- α-D-Talose, R=OH, R'=H; R"=CH₂OH; and the molecule is the mirror image of that depicted.
- β-D-Talose, R=H, R'=OH; R''=CH₂OH; and the molecule is the mirror image of that depicted.

3. Previous Infrared Studies of These Sugars

3.1. Spectra Recorded for the Solid Phase

In 1950, Kuhn [2] recorded the spectra of 10 of the crystalline sugars, each in Nujol suspension, but, except for α -D-glucose (compound 5), he did not mention which anomer was employed. Sugars for which only one anomer is normally available were, presumuly, sugars 1, 2, 21, 25, and the epimer of 17. The other five might have been 4 or 5, 5 or 6, 11 or 12, 13 or 14, and 22 or 23; by comparison of our spectrograms with his, we can now identify the anomers he employed as 4, 5, 11, 14, and 22. For sugars 5 and 14, the spectra were recorded for the range of 5000 to 667 cm⁻¹; for the 8 other sugars, from 1250 to 667 cm⁻¹. For sugar 14, Kuhn also recorded the spectrum of a film of the sugar, obtained by evaporation of an aqueous solution, which was probably either partially or completely equilibrated.

Four years later, the spectrum of sugar 5 ("aglucose"; enantiomer not stated) as a mull in hexachlorobutadiene was recorded [3] for the range of approximately 3500 to 3200 cm⁻¹. In addition. Barker and coworkers [4] discussed bands in the range of 973 to 670 cm⁻¹ shown by the spectra of the following 9 sugars in Nujol suspension: 1, 5, 8, 11, 14, 17, 21(?), 22, and 23. However, the spectra were published in insufficient detail to permit comparison with ours over a wide spectral range. Similarly, in 1957. Konkin and coworkers [5] published the spectra in the range of 3600 to 2700 cm^{-1} for a mull of each of the following sugars (anomer and suspension medium not specified): 1, 5 or 6, 13 or 14, enantiomer of 17. p-fructose, and 22 or 23. In the same year, Farmer [6] published the spectrum of sugar 5 (" α glucose"; enantiomer not specified) in a potassium bromide pellet for the range of 5000 to 625 cm⁻¹. Finally, in 1959, Urbański and coworkers [7] recorded spectra and tabulated bands for 6 of these sugars in Nujol mulls for the range of 4000 to 750 cm⁻¹, but did not mention which anomer (of each) they employed. By comparison of our spectrograms with theirs, we have identified these sugar anomers as 1, 2, 5, 14, enantiomer of 17, and 25. [However, the equilibrium rotation that they recorded for Dribose (sugar 25) is actually that for L-ribose, and their melting point for the n-glucose anomer they examined is closer to that for the β anomer (sugar 6) than for the α anomer (5).]

3.2. Spectra Recorded for the Liquid Phase

Long ago, Coblentz [8] recorded the infrared spectra of **D**-fructose and **D**-glucose monohydrate (sugar 4), presumably as supercooled melts, in the range of 10,000 to 1333 cm^{-t}. Rogers and Williams [9] listed absorption bands (3030 to 960 cm⁻¹) for equilibrated, saturated, aqueous solutions of L-xylose (enantiomer of 1-E), D-glucose (5,6-E), p-lyxose (8,9-E), p-mannose (13,14-E), p-arabinose (17-E), p-galactose (22,23-E), and p-fructose. Next, Barr and Chrisman [10] recorded the infrared spectrum (5556 to 3846 cm⁻¹) of a saturated, aqueous solution of n-arabinose (17-E). For other sugars, they smeared a concentrated aqueous solution of the sugar on a cover glass and heated gently for several hours, obtaining a thick sirup which, they claimed, contained practically no water; after this treatment, each sugar was probably present as its equilibrium mixture. The spectra of these evaporated films (for the range 5556 to 2174 cm⁻¹) were recorded for n-xylose (1-E), n-glucose (5,6-E), L-rhamuose (11,12-E), n-mannose (13,14-E), L-arabinose (enantiomer of 17-E), p-galactose (22,23-E), and **p**-fructose.

Finally, Parker [11] recorded the spectra (for the range of 1667 to 909 cm⁻¹) of 20-percent aqueous solutions (w/v) of L-arabinose (enantiomer of 17-E), p-ribose (25-E), and p-fructose, and of a 10-percent aqueous solution of p-galactose (22,23-E). In addition, he recorded the spectra (for the same range) of 20-percent aqueous solutions of α -p-glucose, β -p-glucose, and β -p-mannose (a) 2.5 minutes

after dissolution, and (b) at the end of mutarotation. By following the change in percent transmittance (at 1143 cm⁻¹ for α - or β -n-glucose, and at 1163 cm⁻¹ for β -p-mannose) with time, he was able to determine the mutarotation constants; these agreed well with those determined from measurements of change in optical rotation (see sec.4).

4. Mutarotational Studies of These Sugars by Optical Rotation

When a crystalline sugar is dissolved in water and the solution is allowed to stand, the optical rotation initially observed may change. An aldohexose or a 2-heptulose, in solution, may adopt one or more of eight modifications. Thus, for an aldohexose in which C-4 and C-5 are both p, the following structures may theoretically be present in the equilibrium solution. Of these, only the aldehydo form will show carbonyl absorption in the infrared spectrum.



For an aldopentose or a 2-hexulose, the septanose forms are impossible, so that, for them, the maximum number of theoretically possible sugar components is six.

It is, of course, possible that the appearance of new species in the solution may be unaccompanied by any change in optical rotation. This would occur if (a) all the species present at any moment have the same optical rotation; (b) the initial and final rotations are the same, but, although Intermediate rotations are different, mutarotation is so rapid that it is complete before observation of optical rotation has been started; or (c) an increase in rotation, caused by appearance (or disappearance) of one or more forms, is exactly balanced by a decrease resulting from disappearance (or appearance) of one or more other forms. In addition, there is the possibility that, at all times during establish-ment of equilibrium, the changes in rotation are so slight as to be virtually unobservable. On the other hand, in some instances, an apparent or spurious mutarotation, caused by a positive or negative heat of solution, might be observed, even though no new species actually appeared in the solution.

When dynamic equilibrium between the forms is reached, the proportion of each that is present in the solution depends on the structural, configurational, and conformational stability of each form.² Some indications as to the proportions of the various forms present in the equilibrium solution of some of the sugars in the present study have been obtained by observing the change in optical rotation, with time, when a crystalline anomer of the sugar is dissolved in pure water. The results * are given in table 2, from which it may be seen that, as regards mutarotational behavior, 4 groups of sugars may be distinguished.

In group 1, exhibiting little or no mutarotation, are the 2-ketoses 2, 7, 10, and 15; the equilibrium mixture for each of these sugars appears to consist almost entirely of one form (possibly the α - or β -pyranose), which may be the same as the crystalline sugar dissolved.

Group 2 sugars (the 2-ketoses 18 and 19, and, perhaps, the 3-ketose 20) exhibit mutarotation, and the equilibrium mixture apparently consists mainly of a single pyranose form together with the α - and β furanose forms.

*A discussion, prepared by H. S. Isbell, of the sugars in solution is given in F. J. Bates and Associates, NBS Circular 440, Chapter XXIX (1942).

TABLE 2. Character of the mutarotation and composition of the equilibrium mixture, as determined by studies of changes of optical rotation

Sugar		Mutarota-	Boulibrium mixture	Refer-	
Name	No,	tion reaction	•	ence	
(7)-1-1340-flexulose	2	slight; complex	almost entirely one form (pyranose) that is the same as for the coverals		
a(?)-D-sinco-Heptukse (?)-D-igro-Herukse	7 10	none none	almost entirely one	23	
(7)-D-manno-Hopfulose	15	none		4	
(?) - D - arabino - Hexulose -0.5 CaCl: 1.5H:O	18	mutarotates	a single pyranose +α-and β-		
3-0-Methyl-(7)-D-arabino- heruloss	19	mutarotates	IUTUL0368	6	
β-D-masteo-3-Heptulose	20	motarotates	7	7	
α-D-X ylose D-Glucost, α.3 D-Drucost, α.3 D-Drucost, α.3 D-Mannost, α.3 (1)-D-Glucos 4.5 CaCl: 0.5 H ₁ O	1 5; 6 8; 0 11; 12 18; 14 15	first order first order first order first order first order first order first order) mainly ∝-pyranose+ ∫β-pyranose	8 8 8 8 8	
β-D-Arabinoso δ-Deory-α-L-galactose D-Galactose, α-;δ β(?)-D-Ribose D-Talose, α-;δ	17 31 22 ; 28 25 96; 27	complex matarotates complex complex complex	&-Dyrances+ β-pyrances+ α-fursnose+ β-fursnose	8 8 8 8,10	

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For group 3 (aldoses 1, 5 and 6, 8 and 9, 11 and 12, 13 and 14, and 16), the mutarotation is a firstorder reaction, and the equilibrium mixture consists mainly of the α - and β -pyranose forms.

The members of group 4 (aldoses 17, 21, 22 and 23, 25, and 26 and 27) exhibit a complex mutarotation, and the equilibrium mixture appears to contain, at least, the α - and β -pyranose forms and the α - and β -furances forms.

5. Discussion of the Spectra

5.1. Spectra of Sugars for Which Both Anomers Were Available

For p-glucose, p-lyxose, L-rhamnose, p-mannose, p-galactose, and p-talose, the infrared spectra were recorded for both of the cystalline anomers. Table 3 lists the bands shown by the α anomer but not by the β anomer of each of these sugars, and table 4 lists the bands shown by the β anomer but not by the α anomer of each. These bands will be discussed in a subsequent article dealing with the infrared spectra of pyranoid sugars.

5.2. Spectra of the Equilibrium Mixtures

In this discussion, the spectrum of the material obtained by lyophilizing the equilibrium solution of a sugar will be referred to as the "equilibrium spec-

TABLE 3. Bands (cm⁻¹) shown by the a anomer but not by the β anomer of eix sugars.

p-Olucose (5)	D-Lyrose(S)	c-Rham - nose-H≰O(11)	o-Man- 2006 (13)	n-Gelao- tose(22)	D-Talcze(26)
*3413 8021 2899		2047 2042 2055 2055	3166 2976 2924	3195 2590 2532	3378 2965 2574
1445 1429 1340 1297	1437	1859 1429 	1453 1885 1297	J447 1325, 1314	1425 1203
1284 1105 1050	1285 1244, 1220 1147	1075	1224 1199 1104	1294 1250 1152 1604 1070, 1045	 1144 1054
- 996 	963 867 862	- 87E - 876 - 830	972 900 915 885 631	997, \$76 • \$58 	952 908
- 6776 821	771 627	858	812, 804 707 679	6756 670	802 715 876
637 635 391	583 549,530 490 476	670 609	609 467 391	4383 800	477
377 347	867 294 	 1801	875 811	345 384, 329 300(?), 292 280	386

trum" for that sugar. It was assumed that, during freezing and lyophilization, no change in composition of an equilibrium solution occurs; for some sugars, this assumption may be unwarranted, and crystallization of a new form, or of the original form, may take place.

The equilibrium spectra all showed a band near 1718 cm⁻¹, suggesting the presence, in every equilibrium mixture, of some of the carbonyl form (aldehydo or keto) of the respective sugar. The intensity of this band differed from sugar to sugar; for example, for p-mannese (13,14–E) and p-galactose (21,22–E), it was quite clearly present, whereas it was weaker for p-fructose (18-E) and p-glucose (5,6-E), and barely perceptible for some of the other sugars. This observation agrees with the results of Lippich [12], who found that the proportion of the carbonyl form present in the equilibrium solution is in the order p-mannose>p-galactose>p-fructose>p-glucose. Similarly, p-manno-2-heptulose (15-E), whose aqueous solution shows [13] an ultraviolet absorption maximum at 2650A, indicating the presence of the carbonyl form, exhibits an infrared absorption band at 1712 cm^{-1} . *D-manno-3*-Heptulose, which is a member of the *p*-arabino series, shows a much stronger carbonyl band (at 1727 cm^{-1}).

The equilibrium spectra of those sugars for which the spectra for both crystalline anomers were available were now studied. These equilibrium spectra were found to fall into 2 groups. In the first group

TABLE 4. Bands (cm^{-1}) shown by the β anomer but not by the a anomer of six sugars.

p-Glucose (6) p-Lyrose (9) t-Rham- nose (12) p-Mau- nose (14) p-Galac- trose (23) 3347 5257	D-Tuloso (27)		
3347 3357	D-Tuloso(27)		
3247 3257 3333 2015 3333 2015 3333 2015 2015 2015 2017 2017 2017 2017 1475 2017 1420 1433 1625 1301 1374 1400 1271, 1203 1200 1200 1105 1166 1170 1106	3497		
3247 5287 3333 2915 3333 2915 111 2874 2874 2857 1473 1584 1473 1453 1425 1361 1374 1410 1371 1318 1371 1271, 1263 1260 1165 1166 1170	8436		
1111 1111 1111 1111 1111 1113 1113 1110 1110 1271, 1203 11105 1106 11170 1106	3247		
2935 2874 2874 2874 2857 1475 2747 1484 111 1475 1477 1484 111 1381 1374 1410 111 1371 1318 1200 111 1371 1318 1200 111 1371 1318 1200 1110 1371 1318 1200 1110	9030		
2874 2874 2857 1475 2747 14584 1420 1453 1425 1361 1374 1453 1425 1361 1374 1410 1311 1318 1311 1271, 1263 1200 1212 1165 1166 1170 1166	2924		
1475 2974 2974 2974 1475 2747 1584 1425 1420 1420 1433 1425 1301 1374 1430 1435 1311 1318 1100 1100 1271, 1263 1105 1166 1170 1269	0000		
1473 2747 1584 1430 1430 1433 1435 1361 1374 1410 1311 1318 1311 1271,1263 1280 1165 1166 1170	2000		
14/30 14/30 14/33 14/35 1361 1374 14/10 14/10 1311 1318 14/10 11/10 1311 1318 12/10 12/10 1371, 1263 11/10 12/10 12/10 11/05 11/06 11/10 12/12	2706		
1331 1333 1430 1433 1410 1331 1374 1410 1 1331 1318 1 1 1271, 1263 1 1 1 1316 1 1 1 1271, 1263 1 1 1 1105 1 1 1	1911		
1351 1374 1410 1331 1338 1381 1271, 1263 1260 1260 1165 1166 1170 1266	1430		
1311 1318 1311 1300 1271,1203 1105 1106 1170 1106	1393		
1311 1318 1311 1271, 1263 1260 1165 1166 1170			
1271, 1263 1280 1280 1271, 1263 1280 1105 1166 1212 1105	1340		
1271, 1263 1299 1289 1165 1166 • 1170 1166	1290		
····· 1165 1166 • 1170 1166	1248		
1165 1166 1170 1166			
	1176		
4001			
Land 1101 Long 1120	10.04		
1062 1100 1069 1069	1074		
1063 LL02			
1038	1032		
1025 1018			
1000	0.04		
	840		
	386		
804 865 10863	879		
7777 7778 7778			
755 729	746		
4/0 0/2 004	000-		
010 010	E 40		
	-04.5		
519 513	4140		
100 101 ····· ····			
416 401 498			
100 400			
040 200			

These bands were mentioned by Urbański and co-workers [7].
 These bands were mentioned by Barker and co-workers [4].

• See footnote b to table 3. • See footnote a to table 3.

TABLE 5. Bands (cm^{-1}) in the infrared spectra of the equilibrium mixtures of four sugars, compared with corresponding bands for each anomer of these sugars.

	D-Clucose L-Rhamnose				n-Mannose			D-Galactore			
5,6-E	5	6	11,19-主	μ	12	15,1 4− E	13	14	22,23-E	22	22
3256 2934 2717 1712	• 3322 2941, 2990 2688	3388 2941 2747	3378 2985 2939 2939 2717 1724(?)	33233 2985 2950, 2899 2703	2976 2918 2695	3375 2941 2907 2747 5 1724	1344 2976 2824 2703		33967 2941 5 1720	33790 2941 —	3413 2950
1647 1420 5 1264 1331	- - -		1650 1456 1478 1385 1230	1899 1449 1429, 1403 1883 1330	 1409 1379 1379 1342, 1323	1418 1885 5 1332	1422 1385 1333	1422 1872 1837	1416 • 1379 1330		1410 1353
1253 1253 1200 • 1147	1234 - 1202 - 1148	1271 1253 1202 • 1165	1208 1229 1176 1140		1259 1235 1166 1149	1259 1911 • 1166	1255 1208	+ 1963 + 1214 + * 1170	1258 1220 1144	— ¹⁹⁶⁰ 1140	1269, 1241 1212 1133
► 1104 1080 	• 1211, 1105 • 1060 • 1026	1111 1082 1035	1125 1087 2066 1018	1122 1096 1070 —	112) 1069 1052 1025	1311 1062 1068 1039 ►1029	1111 1078 1087 	+ 1111 1069 = 1073 1062 1085	1073 1046	1061 1045	1060
8 995 921 901	• 995 • 4 916 		978 904 864	979, 4 976 4 911 4 878	979 909 865	973 955 934 906 870	972 960 		996 949 921 894 879	997, 976 	
840 771 706	• 4 839 • 4 776 	- 709	834 906 776 718 673	4 834 4 905 	836 805 777 718 672	899 808 763 719	831 812 707 		902 796 701	4 792 4 792 707	

See footnote s to table 3.
 These bands were mantioned by Rogers and Williams [9].
 These hands were mantioned by Farker [11].
 See footnote b to table 3.

(see table 5), all bands observed in the equilibrium spectrum (excepting that for carbonyl, at about 1718 cm^{-1}) could be accounted for, either as being (a) distinctive of one anomer present (the bands matching those of one or both of the crystalline anomers) or (b) the resultant of overlapping of neighboring bands displayed by each of the two crystalline anomers, respectively. In this category (for which the equilibrium mixtures consist, presumably, of 3 sugar components, viz, the α - and β pyranose forms and the open-chain form) were the equilibrium spectra of p-glucose (5,6-E), 1-rhamnose (11,12-E), n-mannose (13,14-E), and (except for one hand, at 921 cm⁻¹) p-galactose (22,23-E). For the second group (see table 6), consisting of D-lyxose (8.9-E) and p-talose (26.27-E), the equilibrium spectrum shows bands (besides the carbonyl band) that are absent from the spectrum of either of the crystalline anomers. These extra bands may be attributable to the presence of (a) the open-chain form, (b) one or both anomers of one or more ring-forms different from that in the crystalline anomers examined, or (c) the presence of different conformations of the sugar. It is possible that n-galactose should be included in the second group.

For the other crystalline sugars in table 1, only one anomer of each was available. On comparing

TABLE 6.	Bands (c)	n=1) in the	infrared s	pectra o	f the equilib-
rium n	uxtures of t	noo sugars	, compared	with a	orresponding
bands f	or each anot	ner of these	e sugars.		

	D-Talose	1	D-Lyr039				
27	26	26,27-E	Ð	8	8,9-E 8		
5.55		5742	2200	3500	34455		
000		0000	8267	2000	3050		
2950.2924	29.50	2833	2955	2941	2923		
			2674	2681	2717		
-	_	1724		_	1712(1)		
	1555	273.5	1460	1404	1484		
	1425	1929	1 <u>520</u> 1 9 4 4	1097	1418		
1241	1238	1214	1256	1263	1255		
1176	-	1167					
1(2)	2115	1115	1130	1133	1136		
1089	1085	1092	1107	1099	 1106 1075 		
•	1054	1048	1045	1012	1044		
_	_	996	1006	1006	1005		
<u> </u>	-	908	- 1	-	982		
991	-	637	-	_	945		
870	874	877	883	887	882		
871	-	561	540	843	846		
872	810	810	809	809	806		
765, 746	705	758		771	766		
••••			672	869	672		

· See footnote b to table 5.

the equilibrium spectrum of each sugar with the spectrum of the corresponding crystalline sugar, two groups of spectra were noted. In the first group (see table 7) were the equilibrium spectra³ of L-xylo-hexulose (2-E), D-lyzo-hexulose (10-E), D-gulose 0.5 CaCl₂ (16-E), D-arabino-hexulose 0.5 CaCl₂ (18-E), 3-O-methyl-D-arabino-hexulose (19-E), and p-ribose (25-E); in each of these spectra, all bands which could be clearly distinguished were also present in the spectrum of the crystalline anomer originally dissolved (although the equilibrium spectrum lacked the band-definition of some of the bands displayed by the crystalline anomer). Indeed, for t-xylo-hexulose, p-lyzo-hexulose, and p-ribose, the equilibrium spectrum is scarcely distinguishable from that of the crystalline supar. (In addition, a considerable resemblance between the equilibrium spectra of p-ribose and p-talose is evident, and, in the range of 5000 to 962 $\rm cm^{-1}$, the spectra are almost superimposable.)

The second group of equilibrium spectra (see table 8) consisted of those of p-xylose (1-E), pgluco-heptulose (7-E), *D-manno*-heptulose (15-E), *D*-arabinose (17-E), *D-manno*-3-heptulose (20-E), and 6-deoxy-L-galactose (21-E). Each of these equilibrium spectra clearly showed some bands not displayed by the anomer originally dissolved. New species of each sugar were obviously present in the respective equilibrium mixture; for sugars 7 and 15 (see table 2), a change in optical rotation during equilibration either (a) does not occur or (b) is so slight that it has not been detected. Since, for these 6 sugars, the spectrum of the other anomer of each was unavailable, no decision as to the source of the new bands could be made.

Thus, as regards the composition of the equilibrium mixture, the conclusions earlier arrived at (from studies of mutarotation) agree (or do not disagree) with those derived from the infrared spectra, except for p-lyxose and p-ribose.

A clearcut decision as to agreement between results derived by the two techniques could not be reached for *D-gluco*-heptulose and *D-manno*-heptulose (as a careful scarch for mutarotation has not been made for these sugars) or for *D-gulose*, *D-arabino*-hexulose, and 3-O-methyl-*D-arabino*-hexulose (as their equilibrium spectra were not sufficiently informative).

TABLE 7. Bands (cm⁻¹) in the infrared spectra of the equilibrium mixtures of six sugars, compared with corresponding bands for one anomer of each of these sugars.

L-splo-E	1-1920-Herulose D-1920-Herulose		lexulose	n-Gulose-0.6 CaCl.		D-orabine-Hémilost-0.5 CaCl _a		- 3-0-Methyl-D-arabino- bemices		D-Ribose	
2-E	2	10-E	0L	16-B	LÔ	18-B	18	19-E	19	25-E	25
3890 . 2941 2907 2684	• 3413 2950 2907 2775	8401 3883 2941 2703	8634 8822 2960	33591 25461 27792	3333 2015 2015	3078 1533 2400 2712	8425 3985 2985, 2939	3461 2000 2895	8407 2941 2867	8365 2933 2990 2013	20778 2923 2909 2700
1712 1464 1399		1718 1473 1443 1440	1471 1443 1408	1724(7) 1850 1456 1456	1687 1462 1410	1712 1647 1425	1656 	1712 1468 1410	1481 1435, 1397	1718 1458 1416	1456
1996 1361 1311 1313 1256	1308 1350 • 1312 • 1258	1783 1340 1302 1277 1253	1379 1340 1304 1272 1264	1303 1350	1300 1241	6 1355 1259	1386, 1339 1250	1346	1365	1344	1246
1212 1193 1151 [125	1215 - 1193 - 1161 1125	1241 1185 1155	1239 1171 1163	1147	 1128	1242 1185 1147	1238 1183 1143	1244 1190 1119	1241 7190 1128, 1111	1227 1180 1110	• 1220 • 1130 • 1117
1106 1080 1089 1050 1052	+ 1109 + 1061 1062 + 1049 = 1031	1100 1071 1068 1042	1101 073 1056 1038	1099 1052	1 108, 1085 1057	6 1099 1080 1088 	1112, 1001 1063 1068, 1049	1060	1097 	1085 1044	1085 - 1041
1015 904	1014 - 022	1025 955 947 912	1021 966 947 912	90.7	 963 019	977	 984 920	1000 973 931	904 970 928	1004 989 514	1017 • 959 • 912
000 885 821	+ 901 = 892 + 520	670 822 785	809 822 764	895 853 607	877 878 808	863 822 753	600 823 785	870 825 770	625 831 758	897 870 826 797 747	► 889 - 860 825 > 799 747
721 685	719 683	730 690	731 639		::::				·	724	724

- See footnote a to table 3. - • See footnote b to table 5.

³ The "equilibrium spectrum" of 2,7-anhydro-n-afro-heptulese also belonged to this group, but, as this anhydrids had received a special treatment (see sec. 5.2), the compound is not included here.

p-X3	rlone i	D-giu cs -H	e ptü lcee	D-лалио-2-	Heptukse	p-Ara	tunose	D-Manno-S H	Heptnices 70	é-Deary-r	-galaotoaa
1-E	1	7- B	7	15-E	15	17-E	71	20-IC	20	21– 3 6	21
3355	ь 3833	3366	8418	3356	8403	3256	► 833£	3390- 2976-	3401 2950	3358 2095	3344 3021
2916	2809	2933 2907	2939 2907	2941	2933	2824	2959			2915	2899
2703	2723	2686	2703	2674	2695	2088	2674			2717	2732
1712(?) 1406	1484	1712(7)	-	1712	-	• 1718	_	1727 1653	1658	1718 1464	=
4774	ióói	1464	••••	فتتن	1444	فمنن	jáná	1420	1429	1447	1417
• 1355	1395	1364	1961		1404	1346	1267	1359		1770	1370
1259	· <u>·</u> ··]	1255	1263	j250	1204	1258	⊳ j269	1271	· <u>-</u> -•	1312 1947	1200 1256
1244	> 1236	1000				+ 1218	^b 1238	1247	-	1214	1221
1202	1202	1206 1191	1198 1188	1202	1199	1161		iisi	jisi i	1169	1170
1145 • 1089	• 1149 • 1082	1114	1117 1067, 10 78	i i i i i i	1093.	1139 1025	Ե1185 Ե1098	iidd	1099	1126 1095	1180 1069
				:::::		1065	-	1065	-	1.1.1.	
1057	■ 1055 ■ 1052	1059	1004	1057	1006	1082	• 1087	1052	1060	1096	10/2
1016 \$79	2018	1019 983	1013 296	1025	1021	ióói	s iööi	996		1996	990
		960	-	950	9.52			962		965	963
895 895	► 935 ► 904	907	· <u>··</u> ·	903	906	047 917	* 9465 	902	895	900	-
	-···	879	671			88\$ 990	6 694				•
		832	827	800	· <u>-</u> -·	944 i	▶ <u>844</u>	824	818	000	
812	_			\$22	81B	786	► 786	789	783	814 770	* 819 • 772
709	► 762		·	741	_		· · · · ·			7.58	_
635	· <u>-</u>	716	714	704	702					687	
	-						1	[· · · · ·	

TABLE 8. Bands (cm⁻¹) in the infrared spectra of the equilibrium mixtures of six sugars, compared with corresponding bands for one anomer of each of these sugars.

See footnote b to table 5. These authors studied the chantiomer for 1-B.

Bee footnote a to table 3.
 See footnote b to table 5. Their observations were for the d anomer.

6. Experimental Procedures

6.1. Preparation and Purification of the Compounds

The individual compounds listed in table 1 were prepared by the methods given in the references cited. Each compound was recrystallized from an appropriate solvent until further recrystallization caused no change in its melting point or optical rotation.

For the preparation of 6-deoxy- β -L-mannose (compound 12), 11.1 g of compound 11 was dissolved in 200 ml of boiling absolute ethanol under reflux and the solution was evaporated under diminished pressure to a sirup; the material was freed from water by (4 times) dissolving it in 100 ml of absolute ethanol, adding 100 ml of benzene, and evaporating to dryness. The resulting colorless crystals (10 g) were dissolved in 220 ml of boiling acetone under reflux, and the solution was cooled, to give 5.9 g of a crystalline mixture of the α and β anomers of the anhydrous sugar, mp 114-116°. (Jackson and Hudson had supposed this material to be a compound.) The dry, finely powdered mixture was shaken with absolute ethanol (4 vols.) for 5 min at room temperature, the suspension was filtered with suction (rubber dam), the crystals were im- | losan) monobydrate (compound 24), 0.25 g was dis-

mediately re-extracted in the same way with the same volume of absolute ethanol, and the crystals were rapidly removed by suction filtration (rubber dam) and dried in a vacuum desiccator (Desiguard) over phosphorus pentaoxide at 0.1 mm; the crystals had mp 127–129°

6.2. Preparation of the Equilibrium Mixtures

The crystalline compound (0.5 g) was weighed into a 25-ml volumetric flask, water was added, the solution was made to 25 ml with water, and the specific rotation was observed periodically until mutarotation was complete. For sugars displaying no mutarotation, the solution was kept overnight at room temperature, A portion (0.1 ml) was now transferred, by pipet, to a 5-ml flask containing 500 mg of potassium chloride. The pipet and the neck of the 5-ml flask were washed with water, and the washings were added to the flask contents, which were then brought to about 3 ml with water. The solution was frozen and lyophilized, giving a dry mass containing 0.4 mg (or its equivalent) of the sugar or sugar compound per 100 mg of potassium chloride.

For 2.7-anhydro-\$-p-altro-heptulose (sedohepta-

solved in 20 ml of 1 percent aqueous hydrochloric acid, and the solution was heated, under reflux, in a boiling-water bath for 1 hr. The solution was de-ionized by passage through columns of (a) Duolite $A-4(OH^{-})(20 \text{ ml})$ and (b) a mixture of 2 ml of this resin with 2 ml of Amberlite IR-120 (H⁺), with elution with water until the total volume of final effluent was 125 ml. One milliliter of this neutral effluent was added to 500 mg of potassium chloride in a 5-ml flask, 2 ml of water was added, and the solution was frozen and lyophilized, giving a dry mass containing the equivalent of 0.4 mg of compound 24 per 100 mg of potassium chloride. It should be noted that heating of a 0.07 M solution of sedoheptulosan monohydrate in 0.2 N hydrochloric acid for 1 hr at 100° affords [14] a mixture of 80.4 percent of sedoheptulosan monohydrate with 3.4 percent of 2,7-anhydro-6-p-altro-heptulofuranose, 14.8 percent of *n-altro-heptulose*, and 1.4 percent of 5-(1,2-dihydroxyethyl)-2-furaldehyde.

6.3. Preparation of the Pellets

For spectrophotometric study, samples of the individual compounds were prepared as pellets consisting of the crystalline compound suspended in an alkali-metal halide, exactly as previously described [15]. For the range of 5000 to 667 cm⁻¹, a concentration of 0.4 mg of the compound per 100 mg of potassium chloride was used. The spectrum of compound 20 in this range was also recorded at the same concentration in potassium iodide. For the range of 667 to 250 cm⁻¹, the following weights of compound per 100 mg of potassium iodide were used—compound 25 : 1 mg; compounds 5 and 17 : 1.34 mg; compounds 2 to 4 and 7 : 3 mg; and for the rest of the compounds 16 and 18 in Nujol were recorded at several concentrations.

For the lyophilized, equilibrium mixtures, the dry lyophilizate (already containing the desired proportion of potassium chloride) was pressed directly into a pellet.

6.4. Measurement of Infrared Absorption

The spectrograms are shown in figures 1 and 2. Those in figure 1 for compound 20 and its equilibrium mixture (20-E) were recorded with a Beckman Model IR4 (double-beam) spectrophotometer equipped with prisms of sodium chloride. The others were recorded with a Perkin-Elmer Model 21 (double-beam) spectrophotometer equipped with a prism of sodium chloride (for the range of 5000 to 667 cm⁻¹) and of cesium bromide (for the range of 667 to 250 cm⁻¹), as previously described [15].

Some absorption attributable to water (in the compound, the alkali halide, or both) was observed at 1639 cm⁻¹ and, attributable to atmospheric water vapor, in the far-infrared curves. These regions are drawn on the spectrograms with dashed lines which are not to be interpreted quantitatively.

6.5. Spectra Measured Under Different Conditions

Because of the possibility of interaction of the various sugars with the pelleting halide under high pressure (previously observed [16] for 8 out of 24 aldopyranosides), the spectra of the sugars were also recorded in a Nujoi mull in the range of 667 to 250 cm⁻¹. For 16 of the 27 sugars, the spectra obtained with either medium matched well; for 5, the spectra in potassium iodide were not well defined, but matched those in Nujoi (compounds 8, 9, 15, 16, and 26). However, the following compounds gave spectrograms that were *different* in Nujoi and in potassium iodide: compounds 3, 14, 20, 24, 25, and 27.

In view of these observations, the spectra obtained with a Nujol mull were used exclusively for measuring the positions of absorption bands in the range of 667 to 250 cm⁻¹, not only for the sugars that gave unsatisfactory spectra in potassium iodide, but also (in order to keep the measurements strictly comparable) for the other sugars.

Farmer [6] had noted that, in the range of 5000 to 667 cm⁻¹, " α -glucopyranose" gave a spectrum in potassium iodide that differed from that in potassium bromide. We therefore recorded the spectra of compound 20 (a sugar that gave a poor spectrum in potassium iodide in the range of 667 to 250 cm⁻¹) in potassium iodide and in potassium chloride, at identical concentration in pellets of the same weight, for the range of 5000 to 667 cm⁻¹; the spectrum in potassium iodide was less detailed than that in potassium chloride.

The authors express their gratitude to J. D. Moyer for preparing and lyophilizing the equilibrated solutions. They also thank J. E. Stewart, J. J. Comeford, and F. P. Czech for recording the infrared absorption spectra.



FIGURE 1. Spectrograms of materials in polassium chloride pellets. L. o.D.Xylose; 1-E. D.xylose (equilibrium); 2, (?)-Laylo-bexulose; 2-E. Laylo-bexulose (equil.).



FIGURE 1. Spectrograms of materials in polassium chloride pellels.—Continued 3. arc-glacese-0.5 NoCl-0.5 H2O; 4. arc-glacese monohydrate; 5. arc-glacese; 5. 4-E. Deglacese (equil.).



FIGURE I. Spectrograms of materials in polassium chlorids pellets.—Continued 5, \$-0-glucose; 7, a(1)-0-gluco-heptukse; 7-E, D-gluco-heptukse (equil.); 8, a-D-lynese.

.



FIGURE 1. Spectrograms of materials in polassium chloride pellets.—Continued 2,9-E, D-lynoso (equil.); 9, 9-D-lynose; 10, (?)-D-lyno-bexulose; 10-E, D-lynobauloss (equil.).



FIGURE 1. Spectrograms of materials in potassium chloride pellets.—Continued 11, 6-deoxy-a-L-manness monohydrate; 12, 12-E, 6-deoxy-L-manness (22, e-D-mannes); 12, e-D-manness



FIGURE 1. Spectrograms of materials in polassium chloride pellels.—Continued 13, 14-E. D-mannese (equil.); 14. \$D-mannese; 15. (7)-D-manneseptilese; 18-E. D-manneseptilese (equil.).



FIGURE 1. Spectrograms of materials in polassium chloride pellets.—Continued 18, (7)-D-gulose 0.5 CaOls 0.5 H2O; 18-E, D-gulose 0.5 CaOls (equil.); 17, \$-D-erabinose; 17-E, D-arabinose; (equil.).



FIGURE 1. Spectrograms of materials in polassium chloride pellets.—Continued 18, (?)-D-arabino-bemiose 0.5 CaCh 1.5 H:0; 18-E, D-arabino-bemiose 0.5 CaCh (equil.); 19 3-0-methyl-(?)-D-arabino-bemiose; 19-E, 3-0-methyl-D-arabino-bemiose; 19-E, 3-0-methyl-D-arabino-bemi



FIGURE 1. Spectrograms of materials in potassium chloride pellets.—Continued 39, 5-0-manno-3-beptulose monohydrate; 29-E. D-manno-8-beptulose (equil.); 21, 6-deory-o-t-galactose; A-E, 6-deory-t-galactose (equil.).



FIGURE 1. Spectrograms of materials in potassium chloride pellets, --Continued 22, a-D-galactore; 22, 22-B, D-galactore (equil.); 23, 3-D-galactore; 24, 2,7- anhydro-3-D-akro-heptulose monohydrate.



FIGURE 1. Spectrograms of materials in potassium chloride pellets.—Continued 24-B, mixture from treatment of compound 24 with 1 percent hydrochloric setd; 25, 3(?)-D-ribose; 25-E, D-ribose (equil.); 25, a-D-tekse.



FROME 1. Spectograms of materials in polassium chloride pellets.—Continued 24.27-E. D-talose (equil.); 27, 5-n-talose.

.



FIGURE 2. Spectrograms of materials in Nujel mulls and in polassium iodide pellets. 1. =D-Xylets; 2. (1)-Lepio-hamless; 5. aco-glucose 0.6 NaCl-0.5 H₁O; 4. a-D-glucose monohydrate.



FIGURE 2. Spectrograms of materials in Nujol mults and in potassium iodide pellets.—Continued 5, are-glacose; 5, 6-e-glacose; 7, a(1)-e-glacose; 8, a-e-lyaces.



FIGURE 2. Spectrograms of materials in Nujol mulls and in polassium iodide pellets.—Continued 1. 3-v-lyrose; 10. (1)-v-lyro-berulose; 11. 6-decry-a-t-mannase monohydrate; 12. 6-decry-3-t-mannase.



FLOUBE 2. Spectrograms of materials in Nujol mulls and in polassium iodide pellels.—Continued 18. a-D-mannots; 14. \$\theta-D-mannots; 14. (?)-D-manno-beptules; 14. (?)-D-galass 0.5 CuCh-0.5 HzO.



FIGURE 2. Specirograms of materials in Nujol mulls and in potassium iodide pellets.—Continued 17. \$D-urbinose; 12. (1)-D-gradino-heraloge 0.5 CaOl; 1.5 H2O; 19. 3-O-methyl-(2)-D-gradino-heraloge; 29. \$D-manno-3-heraloge monohydrate.



FIGURE 2. Spectrograms of materials in Nujol mults and in polassium iodide pellets.—Continued 21. 6-decry-a-legalactore; 22. a-D-galactore; 23. a-D-galactore; 24. 2,7-anhydro-8-D-albo-heptulose monohydrate.



FIGURE 2. Spectrograms of materials in Nujel mults and in potassium iodide pellets.-Continued 25, 6(?)-D ribose; 26, a-D-takee; 27, S-D-takee,

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