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Note

Infrared investigations of sucrose in aqueous solutions*

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During the past three years, we have been investigating the possibilities of using Fourier-transform infrared (F.t.i.r.) spectroscopy to characterize different structural isomers of sugars in aqueous media. From these investigations, we have been able to show[1–3] that (*a*) infrared spectra of excellent quality can be obtained in aqueous solvents, (*b*) the vibrational bands characteristic of α and β anomers can be identified, and (*c*) the $^4C_1$ and $^1C_4$ conformations of lyxopyranose can be identified.

Sucrose is known[4] to be a disaccharide made up of α-D-glucopyranosyl and β-D-fructofuranosyl groups. If the F.t.i.r. technique can be used to confirm this fact independently, confidence can be gained in utilizing this technique for solving novel structural problems in the future. Secondly, if the vibrational bands characteristic of the disaccharide link can be identified, the kinetics associated with cleavage of the disaccharide link, in a chemical reaction, can be determined. We now present F.t.i.r.-spectral data for sucrose, and evaluate them in relation to the known structure of sucrose.

The procedure used for F.t.i.r.-spectral measurements was similar to that presented earlier[1–3]. The chemicals used in this investigation were obtained either from Sigma or Aldrich Chemical Co.

In order that F.t.i.r. spectroscopy may be useful as a structural tool, it is necessary that the spectral details of various structural isomers be different. In our earlier articles, the differences in spectral details of the anomers of D-glucopyranose were discussed[2,3]. In the C–H stretching region, the band at ~2940 cm^{-1} was associated[3] with the α, and that at ~2890 cm^{-1} with the β form. Similarly, in the C–O stretching region, the band at ~1085 cm^{-1} was associated[3] with the β form. However, the structural changes associated with D-fructose in H_2O or D_2O result in only small changes in intensity, and the spectral features do not markedly differ for the anomers.

*Fourier-transform Infrared Spectroscopy of Sugars, Part IV. For Part III, see ref. 1.
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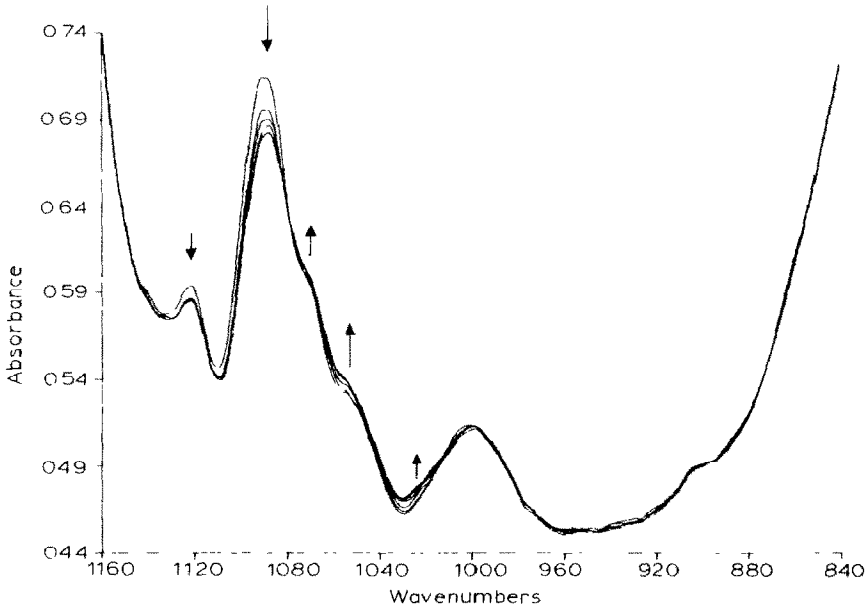

Fig. 1. Time-dependent, F.t.i.r. absorption spectra for β-D-fructose. The first spectrum was obtained at ~60 s after adding D_2O to β-D-fructose. The remaining spectra were subsequently recorded, and the spectral changes were complete within 20 min. The arrows indicate the direction of intensity changes with time.

The time-dependent spectra of β-D-fructose obtained upon dissolving the sugar in D_2O are shown in Fig. 1. In these spectra, and those reported earlier[3] in H_2O as the solvent, the intensity of the band at ~1089 cm^{-1} is seen to decrease, and that at ~1059 cm^{-1} to increase, with time. These major changes in intensity, and other small intensity changes (see Fig. 1), can be associated with the structural isomers that are known[4] to exist in aqueous solutions. However, the overall, qualitative, spectral patterns remain unaffected during the structural changes, and therefore it is not possible to distinguish the anomers of D-fructose from their spectral appearance in this study. A quantitative analysis utilizing the molar absorption coefficients might permit the identification of the percentages of different forms of D-fructose.

These findings restrict our analysis to inquiring if the particular anomer of the D-glucopyranosyl unit in sucrose can be identified. The simplest pathway for this analysis relies on a comparison of the spectrum of sucrose with those of (α-D-glucopyranose + β-D-fructose) and (β-D-glucopyranose + β-D-fructose) mixtures. These mixtures (equimolar components) were weighed out, and their spectra in the 3000–2800-cm^{-1} region, obtained immediately after dissolving in D_2O, are shown in Fig. 2. As the elapsed time between the addition of D_2O and the spectral acquisition was <60 s, the relatively slow conversion between α and β forms of D-glucopyranose is insignificant for the present analysis. Comparison of the spectra in Fig. 2 reveals that the spectrum of sucrose is most similar to that of the (α-D-

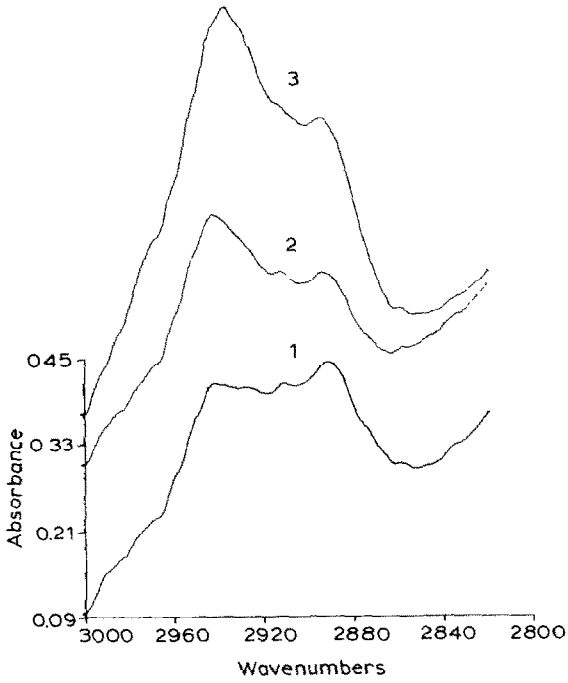

Fig. 2. The C–H stretching region in F.t.i.r. absorption spectra. (*1*) (β-D-Glucopyranose + β-D-fructose) mixture of equimolar components; (*2*) (α-D-glucopyranose + β-D-fructose) mixture of equimolar components; and (*3*) sucrose. The spectra were obtained immediately after adding D_2O to the sample

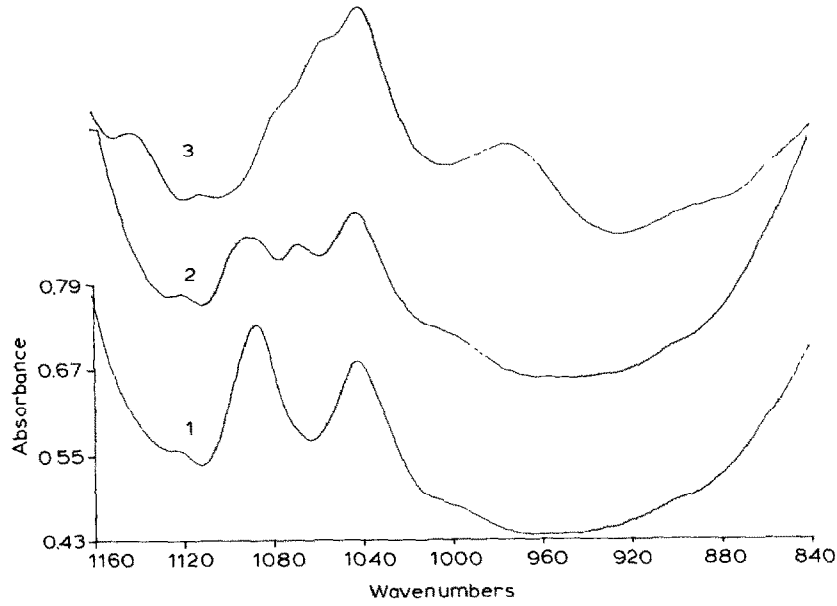

Fig. 3. The C–O stretching region in F.t.i.r. absorption spectra. The labels 1, 2, and 3 have the same meaning as in Fig. 2.

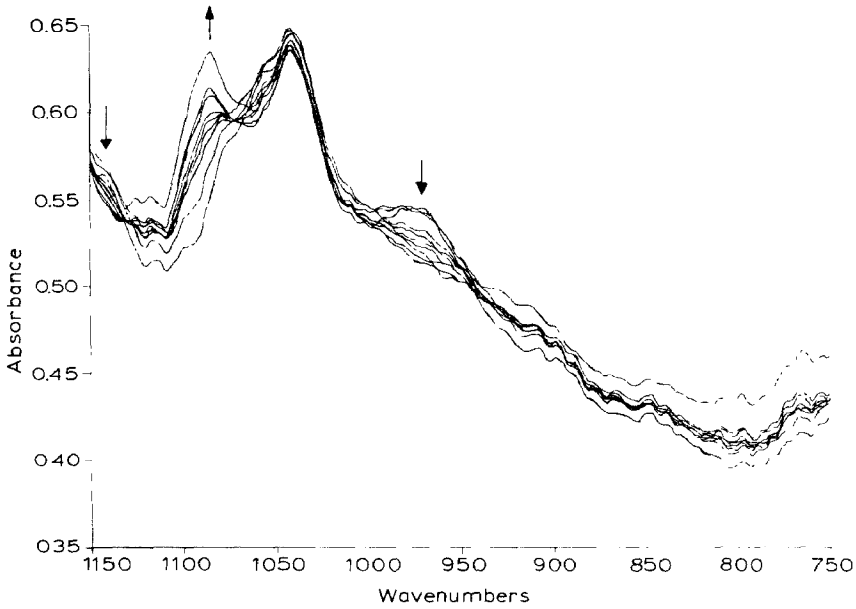

Fig. 4 Time-dependent, F.t.i.r. absorption spectra of 0.3M sucrose in M DCl. The spectra were recorded every few minutes for ~1 h. The arrows indicate the direction of intensity changes with time. All of the spectra were obtained with the sample in a demountable cell equipped with AgCl windows

glucopyranose + β-D-fructose) mixture, in that both spectra contain a large intensity feature at ~2940 cm^{-1}, and a smaller intensity feature at ~2800 cm^{-1}. The ordering of these intensity features is reversed in the spectrum of the (β-D-glucopyranose + β-D-fructose) mixture, which therefore differs significantly from the spectrum of sucrose. A similar conclusion can be reached from comparison of the spectra in the C–O stretching region (see Fig. 3). The spectrum of sucrose is similar to that of (α-D-glucopyranose + β-D-fructose), in that the intensity of the band at ~1040 cm^{-1} is higher than that of that at ~1080 cm^{-1}. The spectrum of (β-D-glucopyranose + β-D-fructose), however, has no similarity to that of sucrose. These findings are in agreement with the known structure[4] of sucrose, and thus the F.t.i.r. technique may prove of immense help in solving novel structural problems.

The differences in the spectral details of sucrose and the (α-D-glucopyranose + β-D-fructose) mixture can mostly be attributed to the influence of the disaccharide link in sucrose, because the differences in the spectral features of the pyranose and furanose forms of D-fructose are less obvious. The broad band at ~975 cm^{-1}, present in the spectrum of sucrose, is not present in that of the mixture. If this band is assignable to the vibrational motion of the disaccharide link, then, during the hydrolysis of sucrose into D-glucose and D-fructose, this band should disappear. To facilitate this assignment, the time-dependent spectra of sucrose in the presence of DCl were recorded; they are shown in Fig. 4. As may be seen Fig. 4, the band at 975 cm^{-1} decreased in intensity and disappeared in time.

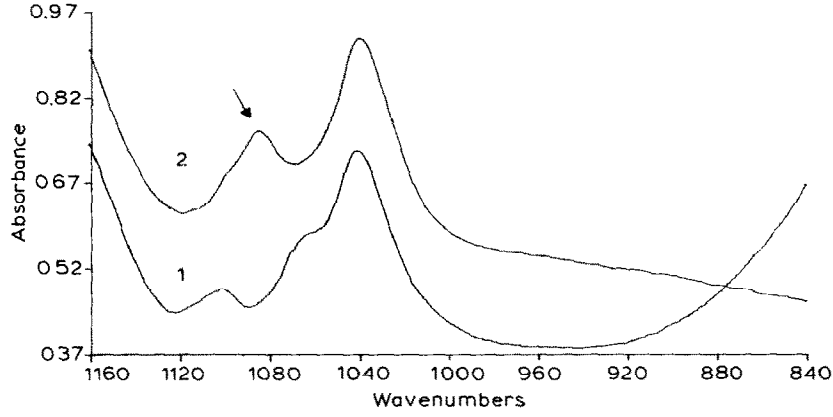

Fig. 5. F.t.i.r. absorption spectra of 0.3M α-D-glucose solution. (*1*) Spectrum recorded immediately after adding D_2O; (*2*) spectrum recorded immediately after adding M DCl. The band at 1084 cm^{-1}, marked by an arrow, is due to the β anomer.

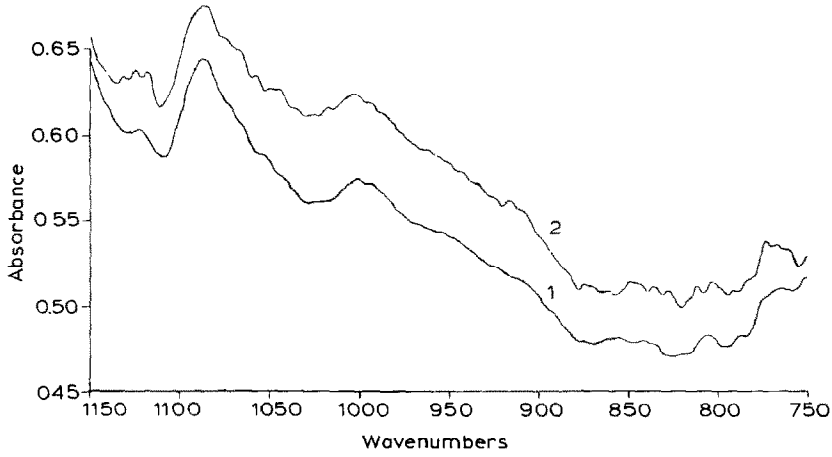

Fig. 6. F.t.i.r. absorption spectra of 0.3 M β-D-fructose solution. (*1*) Spectrum recorded immediately after adding M DCl; (*2*) after 24 h.

It may be noted that this band cannot be associated with the mutarotation of the α-D-glucopyranose and β-D-fructofuranose components liberated, because, at the acid concentration employed, the mutarotation of the liberated components appears to be instantaneous. This information was derived as follows. The spectral changes due to mutarotation in D_2O (in the absence of any acid) can be noticed up to several hours for α-D-glucopyranose[3]. However, the spectrum taken immediately after adding DCl to α-D-glucopyranose shows the band at 1085 cm^{-1}, which is due[2,3] to the β anomer, with considerable intensity, and no further changes in time were noted (see Fig. 5). Similarly, no intensity changes in time were noted in the spectrum of β-D-fructose in the presence of DCl (see Fig. 6). Thus, it may confidently

be stated that the time-resolved, spectral changes seen during the acid hydrolysis of sucrose (see Fig. 4) are due to cleavage of the disaccharide link, and not to mutarotation of the products liberated. These arguments led us to assign the band at 975 cm^{-1} in the spectrum of sucrose to the vibration involving the disaccharide link. The increase in intensity of the band at ~1085 cm^{-1} (see Fig. 4) is attributed mostly to the β anomer of the D-glucose liberated.

The results presented here offer two important points in favor of utilizing F.t.i.r. spectroscopy as a structural tool. One is that the presence of the α-D-glucopyranosyl unit in sucrose could be identified through i.r.-spectral studies in aqueous solvents. This finding offers an analytical procedure for identifying the constituents of a compound of interest. Secondly, the vibrational band characteristic of the disaccharide link was identified, and this permits the reaction mechanisms of disaccharides to be analyzed[5] by using i.r. spectroscopy.

ACKNOWLEDGMENT

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5 P. L. POLAVARAPU, unpublished results. (The integrated absorption intensity changes for the bands at 975 and 1085 cm^{-1} (see Fig. 4) were found to be in agreement with the first-order rate process and yielded a value of 0.0017 s^{-1} for the rate constant.)