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SECOND-DERIVATIVE F.T.-I.R. SPECTRA OF NATIVE CELLULOSES

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ABSTRACT

F.t.-i.r. spectra of algal, bacterial, cotton, ramie, and wood celluloses, obtained in the second-derivative mode, have improved resolution. The spectra support the hypothesis that the crystalline structures of these celluloses can be divided into algal–bacterial and cotton–ramie–wood types. Bands that differ in the spectra of the two types are different from those sensitive to the change cellulose I→II.

INTRODUCTION

The structures of the two major polymorphs (I and II) of cellulose have been studied extensively, but less attention has been given to the question of allomorphy within the cellulose I (native cellulose) family. An early X-ray diffraction study[1] of algal, bacterial, cotton, and ramie celluloses found significant differences in the parameters of the unit cell and differences were observed also in electron diffraction studies[2,3]. Solid-state n.m.r.[4–8], Raman spectroscopic[9], and electron diffraction studies[10] showed that the crystalline structures of native celluloses can be classified into algal–bacterial and cotton–ramie–wood pulp types[5]. Wiley and Atalla[9] proposed that these two types have similar conformations but are packed in different lattices, whereas others[10] have suggested that the differences within the cellulose I family are derived from the size of the unit cells.

I.r. spectroscopy was one of the earliest techniques used to examine the crystalline nature of the celluloses. Marrinan and Mann[11] and Liang and Marchessault[12] obtained two types of band patterns in the OH and CH stretching regions (3600–2800 cm^{-1}) for native celluloses. Marchessault and Liang[13] extended the study to the region 1700–640 cm^{-1}. Despite some of the spectra having been recorded[11] on samples at the temperature of liquid nitrogen, the bands tended to be broad and poorly resolved. However, use of the second-derivative mode[14] can assist in resolving the spectra of celluloses. Second-derivative spectra of celluloses obtained from algae, bacteria, ramie, cotton, and wood are now reported.

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EXPERIMENTAL

The algal cellulose was purified material[15] from the seaweed *Chaetomorpha darwinii*. The bacterial cellulose, supplied in "never-dried" form by Dr. R. Malcolm Brown, Jr., was later freeze-dried; the ramie was a bleached sample provided by Dr. A. D. French. The purification of the cotton and eucalypt wood pulp samples has been described[16].

The samples were dispersed in KBr discs and their spectra obtained by using a Mattson Alpha Centauri F.t.-i.r. spectrophotometer equipped with a water-cooled source, a computer-controlled iris, and a DTGS detector. The spectra were obtained at a resolution of 4 cm^{-1}, are averages of 64 scans, and have been smoothed and differentiated twice[17]. Frequencies were obtained by using the "read cursor", facility.

RESULTS AND DISCUSSION

The even derivatives of profiles of functions describing the shapes of bands in i.r. spectra have the same abscissal value as that of the parent peak but are con-

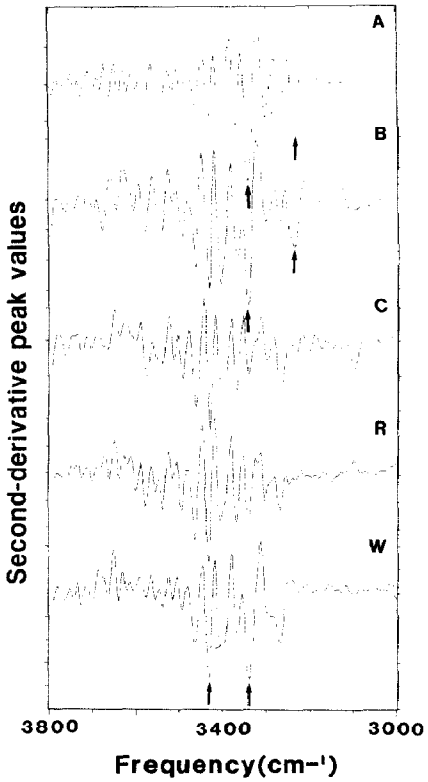

Fig. 1. Second-derivative F.t.-i.r. spectra (3800–3000 cm^{-1}) of native celluloses: A, algae; B, bacteria; C, cotton; R, ramie; and W, wood. Peaks are shown as negative absorbance.

siderably sharper. However, the effect of noise on the profile increases sharply. The use of the second-derivative is a good compromise in carbohydrate spectra[14] but yields "peaks" with negative values of the ordinate.

The OH stretching region of the second-derivative spectra of native celluloses, obtained from algae, bacteria, ramie, cotton, and eucalypt wood, are shown in Fig. 1.

The most obvious difference is the presence of the lowest-frequency band near 3245 cm^{-1} only in the spectra of the algal and bacterial celluloses. This difference has been observed in undifferentiated spectra[11,12] and in the Raman spectra. The band at 3355 cm^{-1} is much stronger in the spectra of algal, bacterial, and wood pulp celluloses than in those of the cotton and ramie celluloses. The bands in second-derivative spectra are dependent on the widths as well as the absorbances of the bands in the parent spectra. Liang and Marchessault[12] found a shoulder at 3450 cm^{-1} in the spectrum of ramie cellulose but not in the spectrum of the bacterial cellulose, and a similar difference was found[9] in the Raman spectrum. This band is present in the spectra of each of the celluloses in Fig. 2, but appears to be relatively weaker in the spectrum of the algal cellulose. Overall, the second-derivative spectra in this region support the proposed types, although the strong band at 3335 cm^{-1} in the wood cellulose is an anomaly. Detailed assignment of the bands is difficult because the number of bands exceeds the number of distinguishable OH groups, which shows that interchain coupling of the OH stretching modes occurs[18]. Also, it is possible that the sharp features produced by resonance interactions between a sub group of the OH oscillators and combination bands are accentuated in the derivative spectra.

Second-derivative spectra of the celluloses in the CH stretching region are shown in Fig. 2. This region of the spectrum of mono-, oligo-, and poly-saccharides has not received much attention and has long been assumed to be little dependent on conformation. However, McKean[19] has shown that CH stretching modes in ethers and alcohols are sensitive to conformation.

The most prominent bands in the spectra in Fig. 2 are those at ~2850 and ~2920 cm^{-1} with the next most prominent band being at ~2970 cm^{-1}. The first two bands have approximately the same relative intensities, but the last band is stronger in the spectra of the algal, cotton, and ramie celluloses and weaker in the spectrum of the bacterial and wood celluloses. Bands at ~2898 cm^{-1} are of medium intensity in the spectra of the algal and bacterial celluloses but weaker in the spectra of the cotton, ramie, and wood celluloses. On the basis of the spectra in Fig. 2, the algal and the bacterial cellulose would be grouped together as would the cotton, ramie, and wood celluloses, but there are differences within each group. Assignment of the bands essentially involves assigning the CH_2 symmetric and antisymmetric stretching modes, as the other bands must arise from CH stretching modes. Because two strong bands occur at ~2850 and ~2910 cm^{-1}, close to the expected frequencies[20] for the CH_2 symmetric and antisymmetric stretching modes, respectively, the bands are assigned accordingly. In the Raman spectrum, the only difference observed between the spectra of algal and ramie celluloses was in the broadness of peaks.

The region 1500–1200 cm^{-1} for the native celluloses is shown in Fig. 3, and there are major bands near 1432, 1370, 1334, 1319, 1284, and 1205 cm^{-1}. What differences there are appear to be confined to the minor bands. The major bands in this region of the i.r. and Raman spectra have been assigned[9,18].

In the spectral region 1200–800 cm^{-1} (Fig. 4), the strongest similarity is between bands in the spectra of the algal and bacterial celluloses. The most significant difference, overall, is in the intensity of a band at ~900 cm^{-1}, which is stronger in the spectra of ramie, cotton, and wood celluloses. Wiley and Atalla[9] found a peak at 913 cm^{-1} in the Raman spectrum of ramie cellulose to be stronger than in the spectra of the algal and bacterial celluloses. Otherwise, the spectra of the plant celluloses differ from those of the algal and bacterial celluloses in the broadness of some bands and, for those of ramie and wood celluloses, in the bands at ~1021 and ~994 cm^{-1}. The band at ~900 cm^{-1} relates to a mode involving the whole group at C-1. This band is doubled in intensity[16] when cotton or wood cellulose is mercerized and is also intensified when cellulose is reduced in crystallinity by ball milling. This

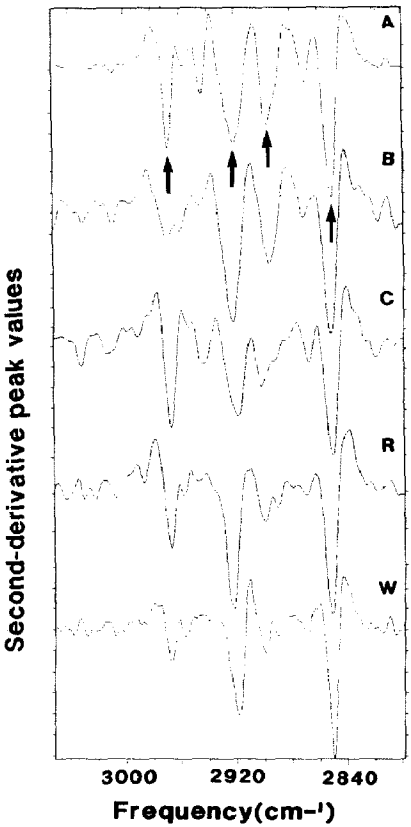

Fig. 2. Second-derivative F.t.-i.r. spectra (3000–2800 cm^{-1}) of native celluloses: A, algae; B, bacteria; C, cotton; R, ramie; and W, wood.

result is consistent with the weakness of the band in the spectrum of bacterial cellulose, the sample of which was highly crystalline[21]. Wiley and Atalla[9] found the intensity of the band at 913 cm^{-1} in the Raman spectrum of celluloses to be inversely correlated with the size of the crystallites.

Spectra in the region 800–500 cm^{-1} are shown in Fig. 5. Bands in this region arise from heavy-atom bending, both C–O and ring modes, with some minor contributions from ring stretching; OH out-of-plane modes may also contribute. The spectra of the algal and bacterial celluloses differ more in this region than at higher frequency, with differences appearing near 784, 716, 615, and 593 cm^{-1}. This finding is not surprising in view of the known sensitivity of bands in this region of Raman spectra to the cellulose I→II transition. Also, there are differences of detail among the cotton, ramie, and wood spectra in this region.

The spectra overall strongly support the grouping of the cellulose structures into two types as noted above. Differences in bands in the OH stretching region (Fig. 1) show that the two types differ in the patterns of hydrogen bonding. Differences in the intensity of the bands at 900 cm^{-1} show that the various samples differ

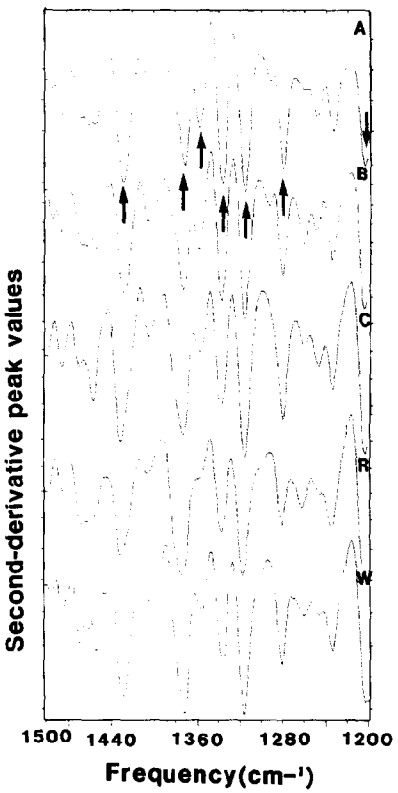

Fig. 3. Second-derivative F.t.-i.r. spectra (1500–1200 cm^{-1}) of native celluloses: A, algae; B, bacteria; C, cotton; R, ramie; and W, wood.

in the size of the crystallites. Differences in the CH stretching region of native cellulose are less than those in the spectra of cellulose I and II[14]. Other bands, known[16] to be sensitive to the transition cellulose I→II, such as those at 1430 and 1111 cm^{-1}, vary little in the spectra of the native celluloses, although some variability is observed for another such band at 990 cm^{-1}. This result confirms that the differences between the native celluloses are unrelated to changes involved in the cellulose I→II transition. Although that transition involves a change in conformation[22], it appears that the differences between the native celluloses cannot be ascribed to differences in conformation.

As expected, the second-derivative spectra of the celluloses show many more well resolved bands than do the parent spectra and provide more information. However, as many of the bands arise from coupled vibrations, decoupling of some modes by deuteration of specific groups is needed for the potential to be fully realized. Of particular interest are the well resolved bands in the CH stretching region, which have received little attention in the past.

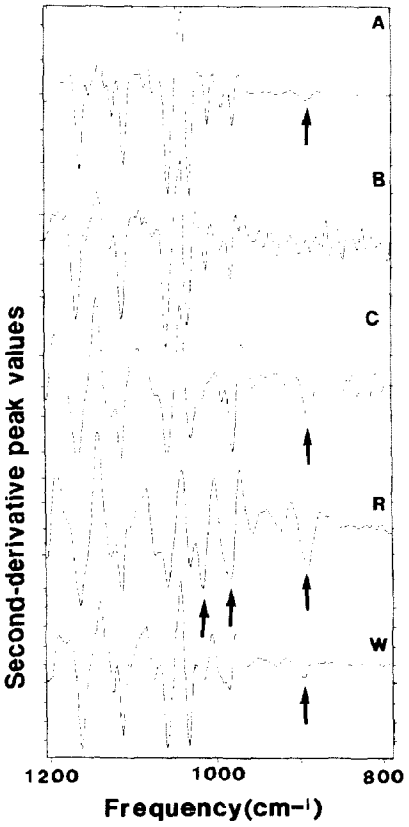

Fig. 4. Second-derivative F.t.-i.r. spectra (1200–800 cm^{-1}) of native celluloses: A, algae; B, bacteria; C, cotton; R, ramie; and W, wood.

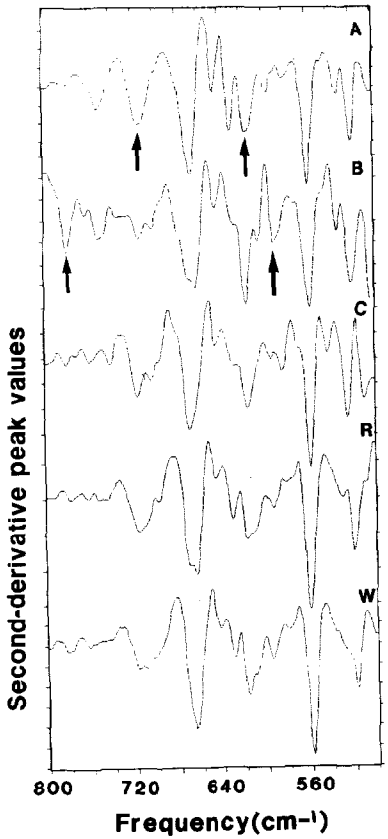

Fig. 5. Second-derivative F.t.-i.r. spectra (800–500 cm^{-1}) of native celluloses: A, algae; B, bacteria; C, cotton; R, ramie; and W, wood.

It is concluded that the grouping of the native celluloses into two types is supported by the second-derivative spectra, with the types differing in patterns of hydrogen banding and size of crystallites but not in conformation as do celluloses I and II.

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