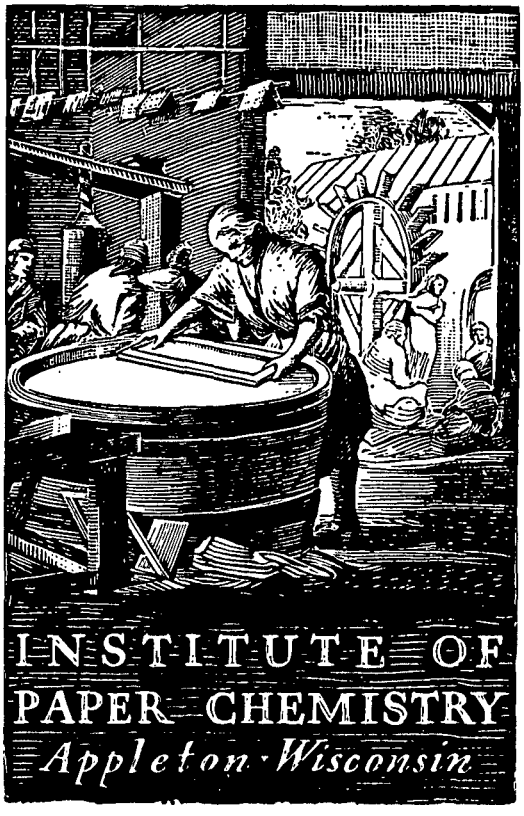

MOLECULAR STRUCTURE AND ORGANIZATION IN WOOD PULP FIBERS

Project 3288

Report Three
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

March 5, 1982

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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TABLE OF CONTENTS

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ABSTRACT

The new model of cellulose structure which we have developed has enabled us to formulate a procedure for quantitative analysis of the structure of cellulosic fibers. This report presents the key observations on which the model is based, together with an overview of the model.

The central features of the model are two distinct linearly ordered conformations of cellulosic chain molecules corresponding to the two most common crystalline forms, I and II; this represents a departure from most prior work. Nonequivalence of adjacent glucose units in the cellulose chains is also a departure from prior models of cellulose structure; it requires that cellobiose be the basic conformational repeat unit along the chains rather than glucose. The differences between the two conformations, which parallel the differences between celluloses I and II, involve occurrence of the nonequivalence at different sites in the two different conformations. In cellulose I it is centered at C-6; in cellulose II it is centered at the glycosidic linkages.

The key steps in the transformation from I to II include disruption of an intramolecular hydrogen bond involving alternate C-6's, and consequent relaxation of the chain into a similar but distinctly different conformation. The similarity of the two conformations leads to their coexistence in most cellulosic materials, with the relative proportions varying with isolation and/or preparation procedures.

Our model of the structures of celluloses I and II is in sharp contrast to those proposed elsewhere which require that conversion from one form to the other involve the rather unlikely transition from a parallel arrangement of adjacent chains in cellulose I to an antiparallel arrangement in cellulose II.

INTRODUCTION

Our major concern since our last report has been development and refinement of a new model of cellulose structure. An integral part of this process has been the emergence of a new view of the differences between the two common crystalline forms, I and II, as well as of the mechanism of transformation between these two polymorphs. The importance of the model derives from new evidence indicating that most wood pulps contain substantial amounts of cellulose II and amorphous cellulose in addition to cellulose I. We have also observed that polymorphic changes occur during processes involved in pulping and papermaking.

As it has long been established in cellulose technology that the chemical and physical properties of the two crystalline forms are quite different, we expect changes in polymorphic content to influence pulp and papermaking characteristics of wood fibers. Measurement of changes in polymorphic distribution, through Raman spectroscopy, provides, for the first time, the possibility of correlating these changes with variations in process variables.

Our new model of cellulose structure is the foundation upon which we have established our new methods for quantitative analysis of polymorphic distribution. We, therefore, devote this report to discussion of the development of the structural model and some preliminary accounts of its application to problems of pulp characterization. More detailed accounts of such application will be presented in subsequent reports.

BACKGROUND

A question of long standing with respect to the structures of cellulose, has been the nature of the polymorphic variability which has been observed in many investigations, both basic and applied, over the years (1,2). The two polymorphs most commonly encountered are cellulose I, usually thought of as the native form, and cellulose II, which is manufactured from the native form by treatment in strongly swelling caustic solutions or by regeneration from the dissolved state.

For many years the most common interpretation of this polymorphy has been in terms of differences in lattice packing of chains of relatively simple structure possessing twofold screw axes of symmetry coincident with the chain axes (3). This is an approximation which was introduced in analyses of x-ray diffraction data, and has been justified as a reasonable simplification in light of the complexity of the structural problem and the limited amount of data available (4,5). Many different structures have been reported on the basis of the assumption concerning symmetry (1). The problem of determining polymer structures and the necessity of assumptions concerning monomer structure and unit cell symmetry have been discussed extensively (6-10).

The results of a number of recent spectroscopic studies of cellulose, utilizing both Raman (11) and solid-state ^{13}C NMR methods (12), could not be reconciled with a model of polymorphy based on the simplifying assumption concerning symmetry noted above. This has led us to reexamine the structural problem for cellulose and to search for models of structure and polymorphy that could reconcile both diffractometric and spectroscopic information. In this report we propose such a model. We believe that, together with the new instrumental methods, the model will facilitate development of quantitative measures of molecular organization and of polymorphic

variations in some of the more complex celluloses occurring in nature or arising in technological processes.

STRUCTURAL VARIABILITY IN CELLULOSE

The pattern of covalent bonding in cellulose is shown in Fig. 1. It was established after many decades of debate and has not been in question since the early 1930's. The outstanding questions, which have been the subject of our research, are concerned with the conformations adopted by molecular chains of cellulose. Examination of the pattern of bonding in Fig. 1 suggests a number of possibilities for conformational variation. Among these, two are of sufficiently low energy to receive serious consideration in our analysis. These are the variability of the dihedral angles at the glycosidic linkage, which define the relative positions of adjacent anhydroglucose rings, and the degree of freedom associated with rotation of the hydroxyl group at C-6 about the C-5, C-6 bond. Variation in the dihedral angles at the glycosidic linkage is severely restricted by hard sphere overlaps among the atoms on adjacent anhydroglucose units. The hydroxyl on C-6, in contrast, can adopt a wide range of orientations. In the crystalline forms, both types of conformational variation are constrained by the requirements of molecular packing in a crystalline lattice.

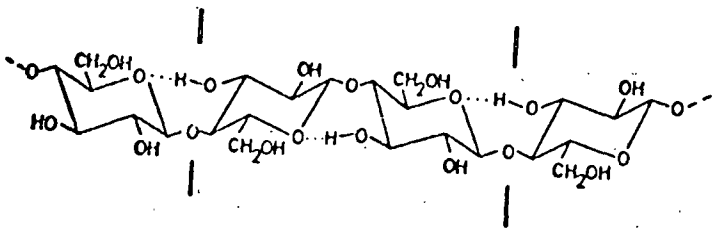


Figure 1. Structure of cellulose.

The primary questions confronting us relate to the subsets of possible linkage and C-6 conformations which occur in the crystalline polymorphs, and the

mechanisms of interconversions between these conformations which can occur during isolation and manufacturing. Later we will also need to consider the degree to which these different conformations can coexist in a particular specimen of cellulose.

In most of the structural analyses based exclusively on x-ray and electron diffractometric studies, the data reduction has rested on assumptions concerning the symmetry of the unit cell. The key assumptions are that the unit cell possesses a twofold screw axis of symmetry, and that this twofold screw axis coincides with the cellulose chain axis (1,3). It is the second of these two assumptions which has implicit in it a number of constraints on the possible structures which can be derived from the data. Since it requires that adjacent anhydroglucose units are related to each other by a rotation of 180° about the axis, accompanied by a translation equivalent to half the length of the unit cell in that direction, it requires that adjacent anhydroglucose units are symmetrically equivalent, and correspondingly that the alternating glycosidic linkages along the chain are symmetrically equivalent. Polymorphic variability has been explained as the result of differences in molecular packing as well as minor variations in the position of the hydroxyl at C-6.

Another option in the analysis of molecular symmetry is to place the twofold screw axis between the molecular chains. This second option, which is equally consistent with the diffractometric data, admits nonequivalence of alternate glycosidic linkages along the molecular chain as well as the nonequivalence of adjacent anhydroglucose units. It has generally been ignored, however, in large part because it requires the introduction of additional degrees of freedom in the refinement of the diffractometric data. Furthermore, it excludes the possibility of the antiparallel alignment of chains in the unit cell.

Our development of a new model for the structure of cellulose was motivated by our conclusion that the spectroscopic evidence, as well as a number of conformational considerations, is not consistent with the degree of regularity implicit in a twofold helix chain structure but requires, rather, that alternate glycosidic linkages be nonequivalent.

DEVELOPMENT OF THE NEW MODEL OF CELLULOSE STRUCTURE

The new model of the structure of cellulose was developed as a result of our effort to reconcile our spectroscopic observations with the prior diffractometric results. In the first detailed assessment of the differences between the Raman spectra of celluloses I and II (Fig. 2) it was concluded that the major differences in the spectra, particularly those in the region below 700 cm^{-1}, could not be accounted for in terms of identical chain conformations packed differently in different crystalline lattices (13). A theoretical analysis also demonstrated that rotation of the C-6 hydroxyl, though it could account for the differences in the spectra below 700 cm^{-1}, would require more significant changes in the region between 700 and 1000 cm^{-1}, which are not in evidence in Fig. 2 (14,15). It was proposed, therefore, that two different stable conformations of the cellulosic chains occur in the different polymorphs. This proposal was also supported by an examination of the spectra of cellulose IV, which appeared to have the same molecular conformations as celluloses I and II, but packed in a mixed lattice.

In search of insight into the nature of the conformational differences suggested by the Raman spectra, the results of conformational energy calculations were examined (16). Two different stable conformations of the glycosidic linkage can be expected; these represent relatively small left-handed and right-handed departures from a twofold helix which are well approximated, respectively, by the experimentally observed conformations in the model disaccharides, cellobiose (17) and methyl-β-cellobiosides (18). It was, therefore, proposed that the chains in celluloses I and II represented sequences of glycosidic linkages in conformations similar to those of methyl-β-cellobioside and cellobiose, respectively. Questions remained, however, about the degree to which molecules with such conformations could

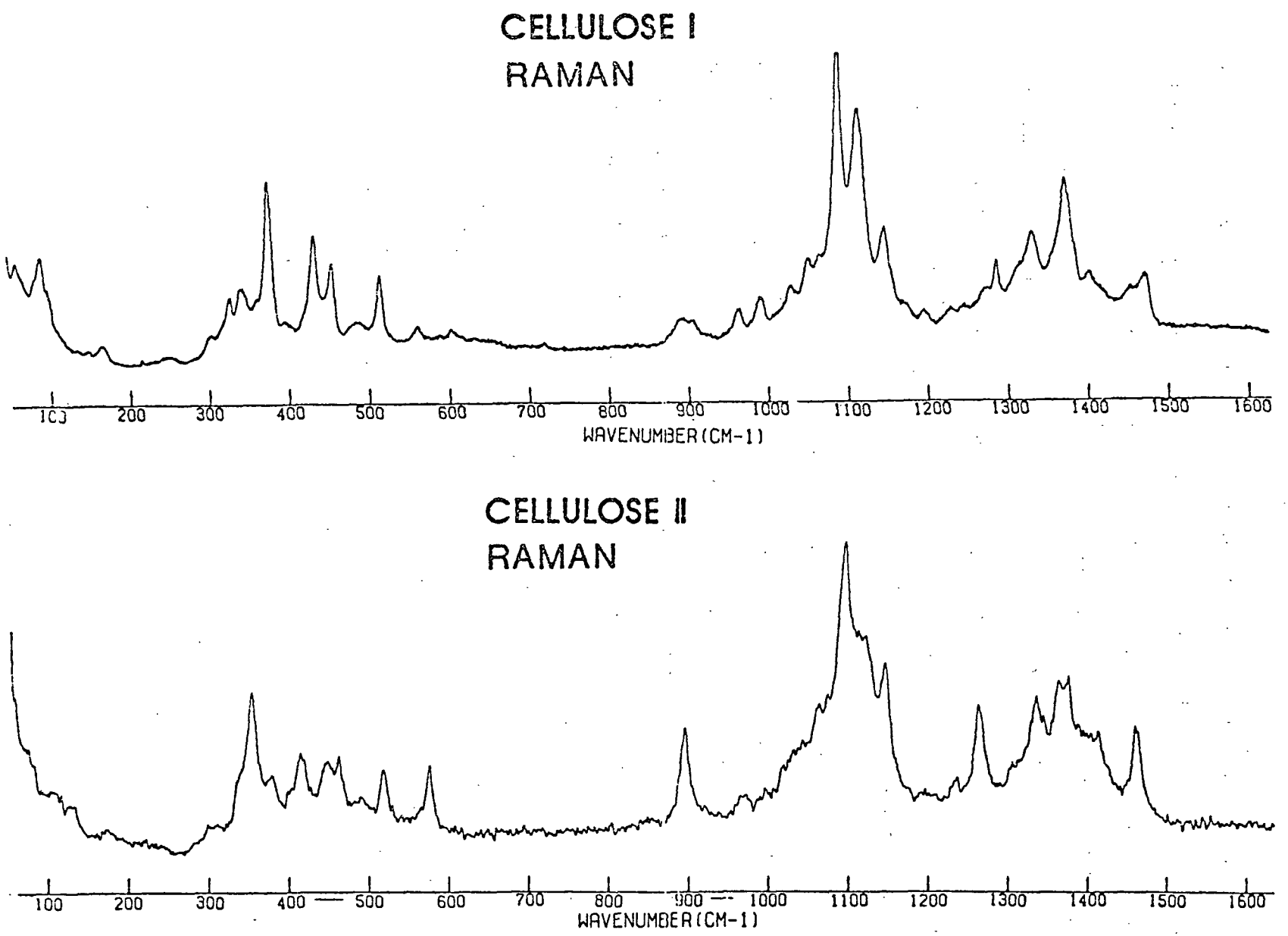


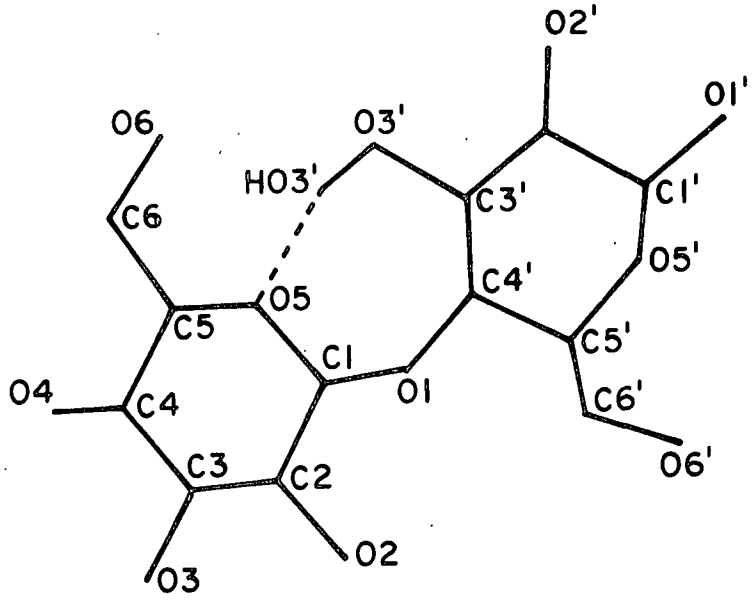
Figure 2. Structures of cellobiose and β-methylcellobioside.

be packed into crystalline lattices consistent with the diffraction patterns observed.

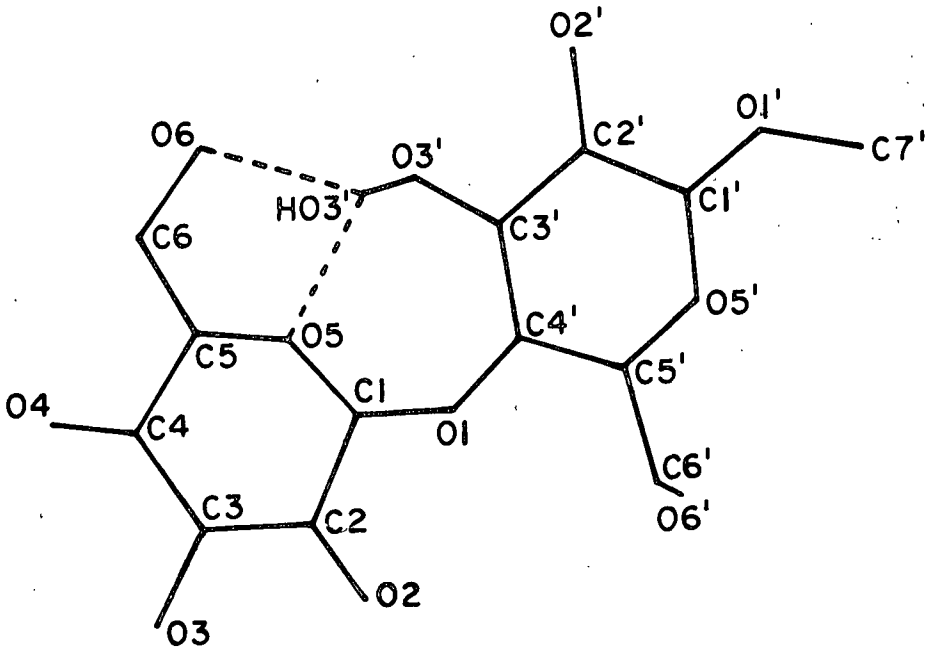
To resolve the questions the comparison with the disaccharides was developed further, with particular emphasis on factors which determine the conformations of glycosidic linkages. Careful examination of the structures of cellobiose and methyl-β-cellobioside (Fig. 3) revealed an interesting difference in the nature of the intramolecular hydrogen bonds between the C-3 hydroxyls on the reducing rings and the ring oxygen of the adjacent rings. These intramolecular hydrogen bonds are important, because they are among the constraints on the freedom of rotation of the anhydroglucose rings about the bonds making up the glycosidic linkage.

In the cellobiose structure the intramolecular hydrogen bond is isolated, whereas in methyl-β-cellobioside it is part of a bifurcated hydrogen bond system also involving the hydroxyl on C-6. It was anticipated therefore that, in the OH region of the vibrational spectra, cellobiose would show a sharp band superimposed on the broader composite band associated with intermolecularly bonded hydroxyl groups. Methyl-β-cellobioside would not have such a band because the bifurcation in the intramolecular hydrogen bond is such that coupling with the lattice modes can occur via C-6. Furthermore, bifurcation in a hydrogen bond results in substantial distortion of the potential surface, compounding the nonlinearities which usually result in broadening of the vibrational bands. The observed spectra were found to be as anticipated (Fig. 4).

Raman spectra of highly crystalline celluloses I and II were recorded in the OH region for comparison purposes. They were consistent with the parallels we have developed between methyl-β-cellobioside and cellulose I on the one hand, and



β CELLOBIOSE



β METHYLCELLOBIOSIDE

Figure 3. Structures of cellobiose and β methylcellobioside.

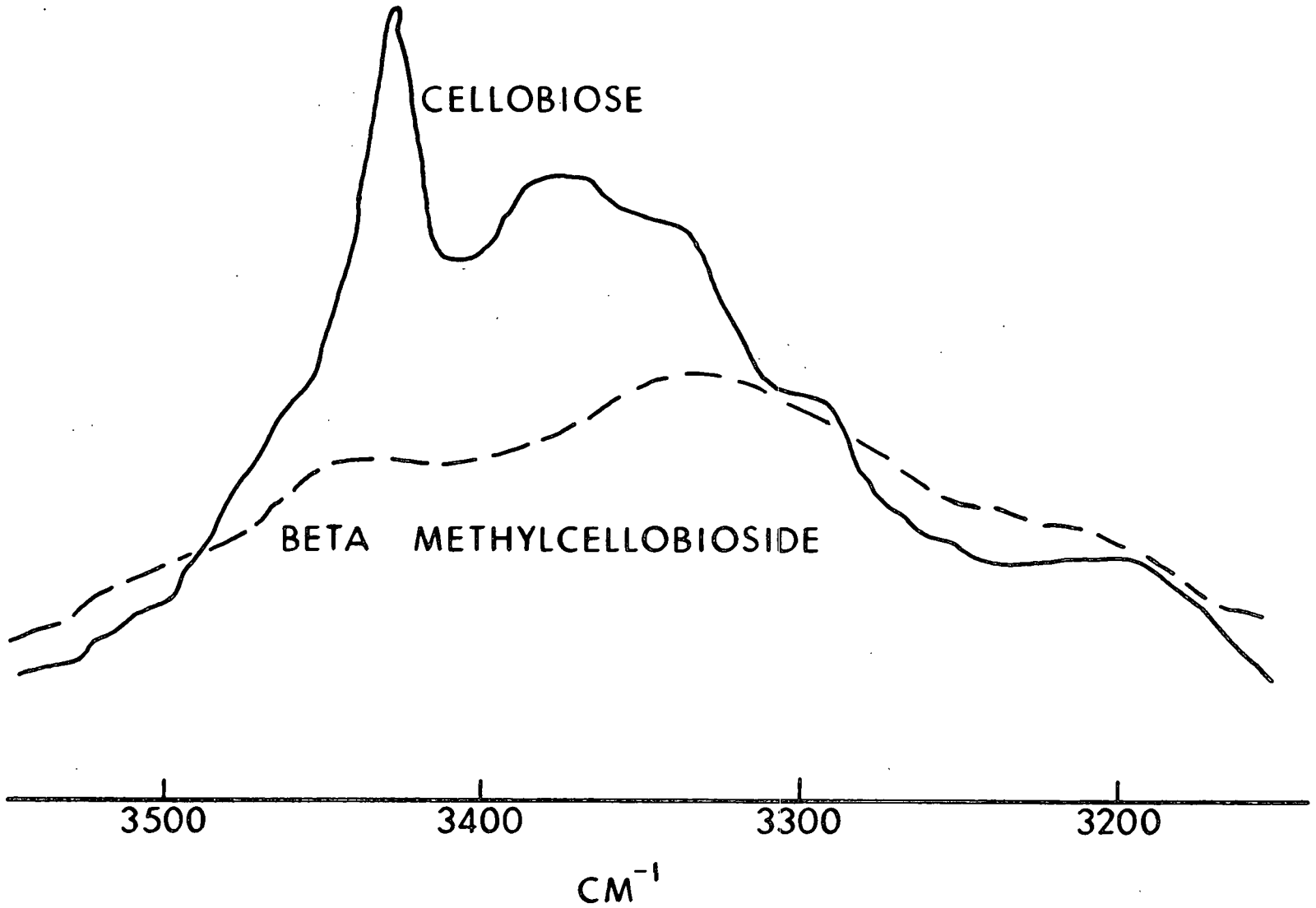


Figure 4. Raman spectra of cellobiose and β-methylcellobioside in the OH stretching region.

cellobiose and cellulose II on the other (Fig. 5). One surprising feature, however, was that cellulose II possesses two relatively sharp bands in the OH stretching region. This feature is also observed in the spectra of the cellodextrins beginning at cellotetraose. After careful reassessment of all available data, these bands were seen as pointing to the possibility of nonequivalent glycosidic linkages, with corresponding differences in the parameters of the associated intramolecular hydrogen bonds (11).

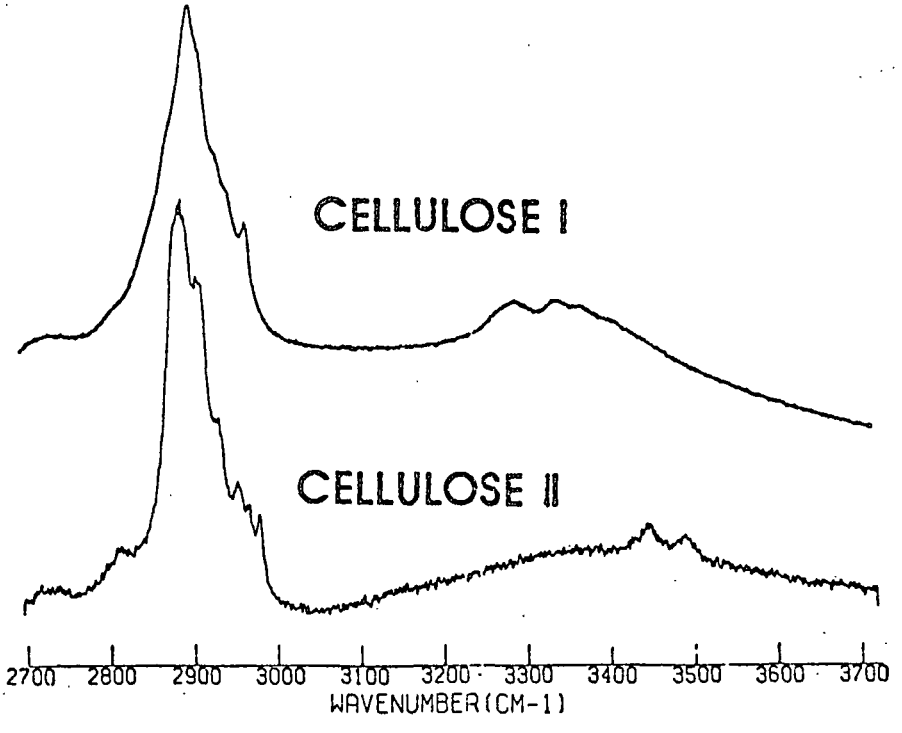


Figure 5. Raman spectra of celluloses I and II in the CH and OH stretching regions.

The possibility of nonequivalent glycosidic linkages was pursued by examination of the solid-state ^{13}C NMR spectra (12). These provided direct evidence of the presence of nonequivalent sets of C-1 resonances and similarly for the C-4 resonances (Fig. 6). These observations leave little question that two types of

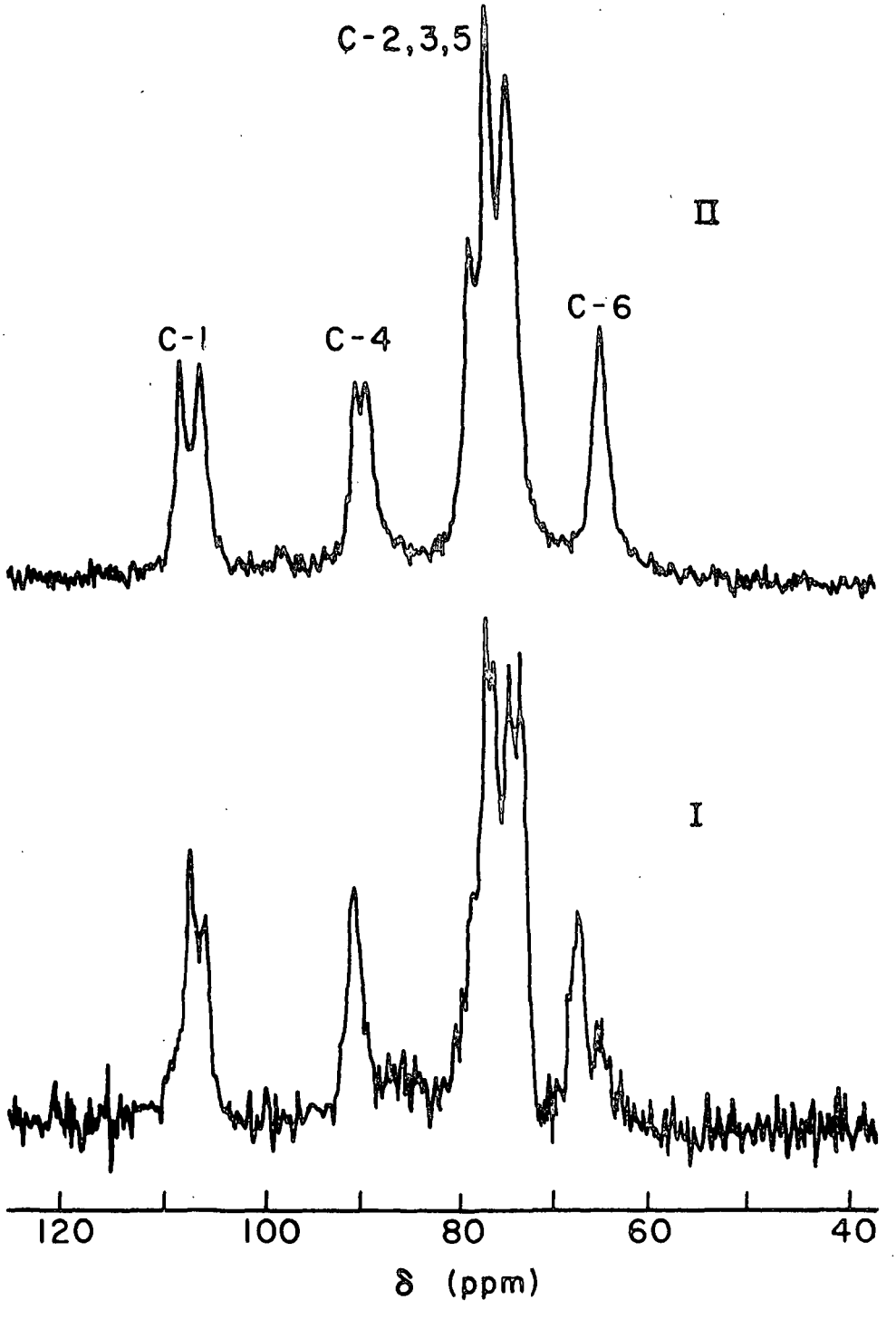


Figure 6. The solid state ^{13}C NMR spectra of celluloses I and II.

glycosidic linkages occur in the cellulosic chains. Furthermore, the differences between ^{13}C NMR spectra of celluloses I and II support the view that two distinct molecular conformations occur in the two polymorphs. The possibility that the NMR spectra are the result of nonequivalent chains in the same unit cell was ruled out on the basis of the x-ray data. Finally the ^{13}C NMR spectra raised the possibility that nonequivalences also occur at C-6, particularly in cellulose I.

The suggestion of nonequivalences at C-6 led us to reexamine the Raman spectra in the region of the methylene vibration wherein some features had remained unexplained for some time. The features were the presence of two overlapping bands, which, however, possess clearly defined heads in the region between 1450 and 1480 cm^{-1} in the spectrum of cellulose I, and their collapse into a single band in the spectrum of cellulose II. These features point to the presence of two nonequivalent sets of C-6's in cellulose I and their merger into a single set in cellulose II.

The model of cellulose structure which emerges from reconciling the different components of spectral and diffractometric data is one which requires a greater degree of conformational variation than is allowed by the assumption, discussed above, that a twofold screw axis of symmetry is coincident with the cellulosic chains, and that the anhydroglucose unit is the basic repeat unit.

THE MODEL IN SUMMARY

In summary the new model of cellulose structure must meet three key requirements not met by previously accepted models. The primary requirement is that celluloses I and II represent different conformations of the chain molecules. Different crystalline lattices are a consequence of the primary differences in conformation.

The second key requirement is that adjacent anhydroglucose units in any cellulose chain are nonequivalent. Hence the basic repeat unit in crystalline celluloses must be taken to be the dimeric anhydrocellobiose unit.

The third requirement is that the differences between the structures of celluloses I and II arise from the character of the nonequivalences between adjacent anhydroglucose units; the conformational differences responsible for the nonequivalences are centered at different locations. In cellulose I the C-6 hydroxyl groups on adjacent anhydroglucose units are the centers of nonequivalence. The glycosidic linkages between successive anhydroglucose rings are also nonequivalent in cellulose I, although they are not as distinct as in cellulose II. In cellulose II, on the other hand, the nonequivalence is centered at the glycosidic linkages, while the C-6's appear to be essentially equivalent for adjacent anhydroglucose rings.

The requirements set forth above can be met only by selecting the alternate option for the symmetry of the unit cell, that is, the option placing the twofold screw axis between the cellulosic chains. As suggested earlier, a corollary of this placement of the twofold screw axis is that the molecular chains are parallel in both celluloses I and II.

When, in addition to the requirements set forth above, considerations of chain packing in the lattice are accounted for, a picture which suggests itself is

one based on incorporation of characteristics of both experimental disaccharide structures. The model that we propose is one of a cellulose chain with alternate glycosidic linkages approximately similar to those in cellobiose and methyl-β-cellobioside. That is, they are alternate left-handed and right-handed departures from the twofold helix structure. This feature is taken as common to both polymorphic forms.

The basic difference between the two polymorphs appears related to the nonequivalence of the C-6's in cellulose I. On the basis of the vibrational spectra in the OH stretching region, we believe that alternate C-6's in cellulose I have their primary hydroxyl group participating in a bifurcated intramolecular hydrogen bond similar to the pattern observed in methyl-β-cellobioside. Participation of the alternate primary hydroxyls in this bifurcated intramolecular hydrogen bond is considered to be the primary factor stabilizing glycosidic linkages in cellulose I in positions where their nonequivalence is less distinct than in cellulose II.

In the context of our model the mechanism of conversion of cellulose from polymorph I to polymorph II appears relatively simple. It corresponds to disruption of participation of the primary hydroxyl group on every other C-6 in the bifurcated intramolecular hydrogen bonds. This would then allow the glycosidic linkages to relax into the more distinct positions characteristic of cellulose II, and permit the C-6's to move into approximately equivalent positions. The contraction of the unit cell in the chain direction upon conversion of cellulose I to cellulose II appears to be one consequence of relaxation of the glycosidic linkages.

Our model for conversion from cellulose I to cellulose II is in sharp contrast to those proposed elsewhere, which require that the change represents a

transition from a parallel arrangement of adjacent chains in cellulose I to an anti-parallel arrangement in cellulose II; this requirement of some previous models has resulted in much skepticism concerning structures derived from diffractometry alone.

WOOD PULP FIBERS

For some time now we have confronted the observation that Raman spectra of fibers from woody tissue contain a number of features characteristic of cellulose II. This, of course, is in contradiction to the rather general belief that native celluloses are of the (I) form and that variations in the resolution of their x-ray diffractograms represent different degrees of crystallinity.

The Raman spectra led us to reassess interpretation of the x-ray diffractograms. On the basis of a more critical analysis, it is now clear that the x-ray data can equally well be interpreted as reflecting a structure in which the (I) form is dominant, although a substantial minor component of the (II) forms is present.

We have also established that the distribution of the cellulosic components of wood pulp fibers between the (I) and (II) forms is quite sensitive to isolation procedures. Thus, fibers derived by pulping at low temperatures possess higher amounts of the cellulose II component. Kraft pulps from the same wood source have the (II) fraction substantially reduced. We believe that such variations provide a basis for understanding some of the differences between pulps isolated under different conditions.

In our continuing studies we have developed methods for quantitative characterization of the polymorphic composition of wood pulp fibers. These have been applied to characterizing differences between kraft and sulfite pulps, and their response to different treatment conditions. The results, which were part of the Master's research program of J. Ranua (19), suggest that a primary difference between kraft and sulfite pulps is the presence of a limited amount of cross-linking in the kraft pulps.

REFINING EXPERIMENTS

In our preliminary studies on refining, Raman spectra were used to assess the degree to which molecular level dispersion occurs during the refining process. A southern pine bleached kraft pulp was refined in a PFI mill to approximately 300 CSF. A portion was then freeze-dried and pressed into a pellet for spectroscopic studies. An unrefined control sample was prepared in the same manner. The spectra are shown in Fig. 7. The small increase in the intensity of the band at 355 cm^{-1} in the spectrum of the refined sample suggests an increase in the cellulose II fraction in the refined pulp. It is clear that the fraction of cellulosic substance which underwent conversion from the (I) form to the (II) form must have been solvated or swollen at a molecular level for the transformation to have taken place. A limited amount of dispersion at the molecular level appears inevitable in refining.

Our preliminary studies of refining have recently been extended to include quantitative characterization of the degree of polymorphic conversion upon refining. Experiments have been carried out with wood pulp fibers as well as with highly crystalline cotton-derived celluloses. In all cases they clearly demonstrate the conversion of cellulose I to cellulose II or the amorphous form, and are consistent with dispersion at the molecular level during refining. These studies are to be completed in the near future and will be the subject of a separate report.

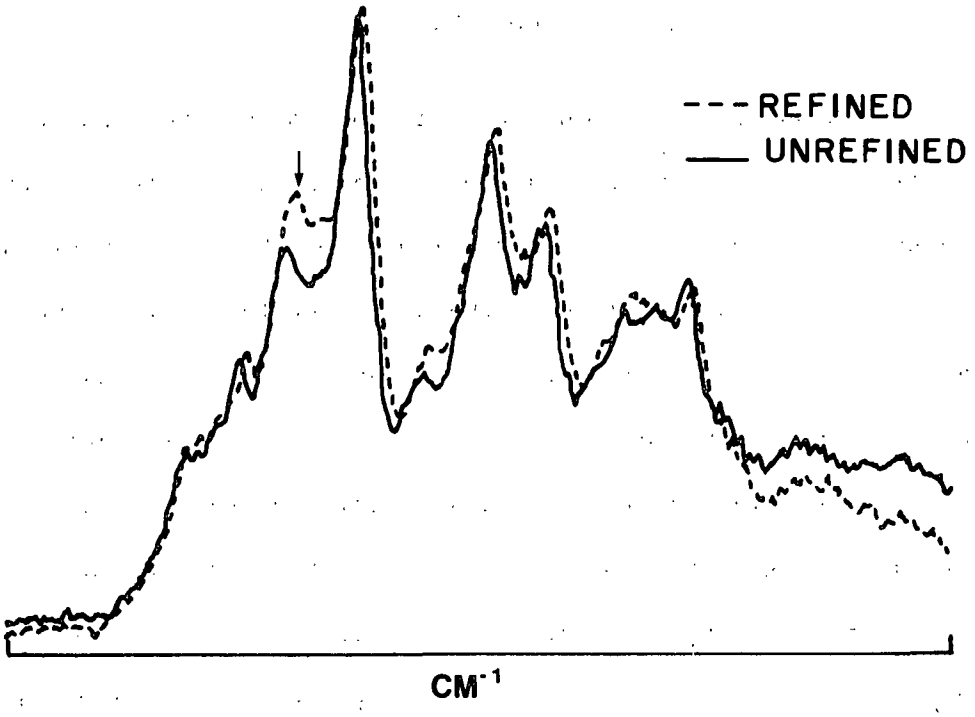


Figure 7. Raman spectra of refined and unrefined kraft pulp in the skeletal bending region.

CONCLUSIONS

We have proposed a new model of cellulose structure based on a repeat unit of anhydrocellobiose in which the adjacent anhydroglucose units are not equivalent. The twofold screw axis believed to be an element of the symmetry of the unit cell must, therefore, lie between molecular chains rather than coincident with them. Such a model allows an internal degree of freedom to the conformation of the cellulose chain, associated with variation in the sets of dihedral angles defining the glycosidic linkages. Intimately coupled with this internal variability is the capacity of the hydroxyl group on C-6 to participate in a bifurcated intramolecular hydrogen bond similar to that in methyl-β-cellobioside. These internal degrees of freedom taken together are shown to be centrally involved in polymorphic variations in cellulose.

The model provides a rationale for observation of spectral features associated with both polymorphic forms in native fibers. It also provides a basis for understanding the redistribution between these forms as a result of isolation procedures as well as refining.

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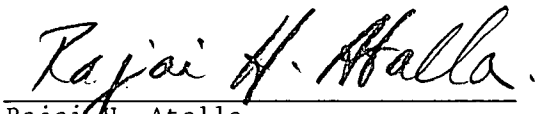

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