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METHOD TO CELLOTETRAOSE

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FINAL REPORT
Cooperative Agreement No. 58-7830-564
between Southern Regional Research Center, USDA and Georgia Institute of Technology
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ABSTRACT

The Rietveld method of structure refinement from x-ray powder diffraction data was applied to cellotetraose, which gives a diffraction pattern similar to that of cellulose II. Unit cell dimensions were consistent with earlier work. The space group was shown to be P1 rather than P2₁. Models, rigid except for the positions of the O(6) atoms, were used to test the effects on the calculated diffraction patterns of parallel and antiparallel packing modes, O(6) positions, and the presence of hydrogen atoms. The hydrogen atoms had a negligible effect on the calculated x-ray diffraction pattern. The intensities of specific individual Bragg reflections were sufficiently affected by the O(6) positions so that they may help to indicate those positions, even though the net effect on the overall pattern-fitting was small. Results from refinement of an antiparallel model against intensities calculated from a parallel model indicated that differentiation should be possible on the basis of high quality x-ray powder diffraction patterns. Preliminary results based on simple models with tetramer symmetry close to 2₁ suggested that the two tetramers in the unit cell are parallel and both are slightly inclined to the c axis.

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INTRODUCTION

It has long been known that cellotetraose, the β 1,4-linked tetramer of D-glucose, yields a powder diffraction pattern exhibiting more crystallinity but otherwise similar to that of cellulose II, the allomorph resulting from treatment of cellulose I in strongly alkaline solution or from regeneration from solution. In the quest to obtain structural information applicable to cellulose II, previous workers, using tiny single crystals, e.g., 0.2 x 0.1 x 0.01 mm$^3$ "usually of poor quality but with well developed (001) faces" \(^{(1)}\), suggested \(^{(2)}\) that the space group of cellotetraose was P1 and determined the unit cell of cellotetraose accordingly. Further single-crystal diffraction work has, however, been thwarted by x-radiation damage occasioned by the long exposures required because of the small size of the crystals.

Rietveld refinement \(^{(3,4)}\) permits structural study with powder diffraction data. The entire diffraction pattern is calculated from a model consisting of the unit cell parameters, crystallite size (line width), proposed atomic positions and thermal parameters. The validity of the proposed model is measured by comparison of the observed and calculated intensity at each step-scan increment, including background correction, and the model parameters are systematically refined in order to provide the best agreement in a least squares sense.

In Immirzi's method \(^{(5)}\), the molecule is described in terms of generalized coordinates so that the model can be refined when the data are limited and the molecule is complex. This is similar to the analyses of fiber diffraction data in which the monomers are kept rigid except for rotating side groups. However, powder diffraction data are less likely to
be affected by errors in collection, correction and reduction than fiber data. Errors from preferred orientation produced in sample preparation are possible, but can be tested for.

Although the Rietveld method has been used successfully with hundreds of materials, including some polymers such as polypropylene (6), it is believed that this is the first attempt to perform a thorough structural study of an oligosaccharide with powder x-ray diffraction data. In this paper, we describe some of the details of the Rietveld method, as modified by Immirizi for polymers and further modified locally, and discuss our assessments of various assumptions used in such a study. A preliminary structural result is also presented.

**EXPERIMENTAL PROCEDURE**

The samples of cellotetraose studied herein were provided by Dr. Fred Parrish, Southern Regional Research Center, Dr. Ross Brown, University of Florida, and Dr. John Vercellotti, V-Labs, Covington, LA. They were made by hydrolysis of cellulose in hydrochloric acid and separated from the other resulting oligomers through column chromatography.

The step-scanned, wide-angle diffraction data were obtained (reflection mode) with a standard θ-2θ x-ray powder diffractometer using a diffracted beam monochromator and CuKα radiation from a standard sealed-off x-ray tube. The scanning range was from 7° to 43.40° 2θ; no clearly recognizable peaks were observed beyond 43.40°. The step width was 0.04° and the counting time was 250 seconds per step. Since little improvement in the data resulted from maintaining the specimen near liquid nitrogen temperatures all results reported here were obtained from room temperature data.

The absorption factor exp(−μt) (equal to Itransmitted/Iincident, for a
normally incident beam) was measured as 76.4% and the experimental data were corrected for specimen transparency with this factor according to, $I_{\text{corrected}} = I_{\text{obs}}(1 - \exp(-\mu t / \sin(\theta)))$. The wide-angle diffraction pattern is shown in Figure 1. Small-angle data were collected with a small angle x-ray diffractometer equipped with a position sensitive detector placed 25.0 cm. away from the sample (transmission mode). The result is shown in Figure 2.

Rietveld Refinement Method

Given the atomic positions from a model, the intensity $y_i$ at the $i^{th}$ step is

$$y_i = y_{i,b} + \sum y_{i,H}$$

$$y_{i,H} = G(\theta_i - \theta_H) |F_H|^{2P_H T_H (LP)_i}$$

where

- $y_{i,b}$ = background at the $i^{th}$ step
- $H$ = Miller indices $h,k,l$ for a Bragg reflection
- $G(\theta_i - \theta_H)$ = Bragg reflection profile function (a Pearson VII function was used, see references 4 and 6 for more details)
- $\theta_i$ = scattering angle at the $i^{th}$ step
- $F_H$ = structure factor
- $P_H$ = multiplicity of $H$
- $(LP)_i$ = Lorentz and polarisation factor at step $i$
- $T_H$ = $\exp(-P(\alpha_H)^2)$, preferred orientation function
- $P$ = preferred orientation parameter
- $\alpha_H$ = acute angle between the preferred orientation direction and the reciprocal lattice vector for $H$

The background intensity ($y_{i,b}$) is calculated as

$$y_{i,b} = b_1 + (b_2 - b_1)(2\theta_i - 2\theta_1)/(2\theta_1 - 2\theta_2)$$
\[ + b_3 \cdot G(2\theta_3 - 2\theta_1) \]

where

\[ 2\theta_1 \text{ and } 2\theta_2 \text{ are the limits of the scanning range,} \]
\[ G(2\theta_3 - 2\theta_1) \text{ is a Pearson VII function with 3 refinable parameters, and} \]
\[ b_1, b_2, b_3, 2\theta_3 \text{ are also parameters that are refined.} \]

The equation given above for \( y_{ib} \) is empirical and a graphical representation of it can be found in reference 6.

The structure factor \( F_H \) is calculated as follows:

\[
F_H = \sum_{j} M_j f_j \exp\{-2\pi i(hx_j + ky_j + lz_j)\} \exp\{-B_j(d_H^*/2)^2\}
\]

where \( j \) ranges from 1 to no. of atoms in the unit cell

\( M_j \) = site occupancy (of the \( j^{th} \) atom site)

\( f_j \) = atomic scattering factor for the \( j^{th} \) atom

\( x_j, y_j, z_j \) = fractional coordinates of the atom \( j \)

\( B_j \) = temperature factor

\( d_H^* \) = \( 2 \sin\theta/\lambda \)

\( \lambda \) = wavelength of the radiation used

The difference between the observed and calculated patterns is measured by the residual

\[
\chi^2 = \sum w_i(y_{i,obs} - y_{i,calc})^2 \tag{1}
\]

where the sum extends over all scattering angles \( 2\theta \) at which a measurement of the diffracted intensity \( y_{i,obs} \) was made. \( w_i \) is a weight factor, usually chosen to be \( 1/y_{i,obs} \). A minimum in \( \chi^2 \) is sought. A necessary condition for termination of refinement is that the gradient of \( \chi^2 \) with respect to each of the \( M \) refined parameters, \( x_k \), has vanished. The resulting equations are nonlinear in the \( x_k \)'s and cannot be solved analytically for the parameter shifts \( dx_k \) which will minimize \( \chi^2 \). Therefore, the calculated intensities are expanded in the \( x_k \)'s and only
linear terms are kept. Letting braces denote matrices and parentheses denote vectors, one ends up with an equation of the form

\[ \{A\} \begin{pmatrix} dx \end{pmatrix} = \{b\} \]  

or

\[ \begin{pmatrix} dx \end{pmatrix} = \{A\}^{-1} \{b\} \]  

The various quantities are:

\[ A_{jk} = \sum \frac{w_i \delta y_i,\text{calc}}{\delta x_j} \frac{\delta y_i,\text{calc}}{\delta x_k} \]  

\[ b_j = \sum w_i \frac{\delta y_i,\text{calc}}{\delta x_j} (y_i,\text{obs} - y_i,\text{calc}) \]  

\[ dx_k = x_k^{\text{old}} - x_k^{\text{new}} \]

This clearly shows several important features of the Rietveld refinement procedure. Firstly, it involves inversion of an M*M matrix. Secondly, it works only if the starting values are already close to a minimum, because of the linear approximation in the derivation of equation (2). Thirdly, whatever minimum is obtained, it is not necessarily the global minimum one is looking for but may be a local minimum, since the method is a local one. Finally, because of finite width of every reflection, the calculated intensity at each step contains contributions from several neighbouring reflections. In our case up to 45 possible reflections can contribute to the intensity calculated at a single point in the diffraction pattern. The program used for Rietveld refinement in this work is a locally modified (extensively) version of REFIN (FORTRAN V), written by A. Immirzi (5).

In order to assess the agreement between the calculated and observed pattern, several numbers can be calculated. Most commonly used are \( R_{wp} \) and
\[ R_{wp} = \left[ \frac{\sum w_i (y_{i,obs} - (1/c) y_{i,calc})^2}{\sum w_i y_{i,obs}^2} \right]^{1/2} \]  

(7)

and

\[ R_p = \frac{\sum |y_{i,obs} - (1/c) y_{i,calc}|}{\sum y_{i,obs}} \]

(8)

where \( c \) is a scale factor. On a strictly statistical basis \( R_{wp} \) is the preferred indicator, because its numerator is the function that is being minimized (equation 1). Note that these \( R \) values are normally larger than those reported for fiber and single-crystal studies because they are based on the intensities at all steps in the pattern and not just on individually observed Bragg reflection intensities.

Another indicator can be calculated which is more akin to the conventional 'R value' with which some readers will be familiar from the literature on single crystal structure refinement:

\[ R_B = \frac{\sum (I_{i,"obs"} - I_{i,calc})}{\sum I_{i,"obs"}} \]

(9)

In its formulation, \( R_B \) is comparable to the conventional \( R \) value based on intensities which, for a normal distribution of errors, is larger than the most quoted \( R \) value based on structure factors by a factor of \( \sqrt{2} \).

In equation 9, \( I_{"obs"} \) is written with quotation marks because it is not actually observed directly. Rather, the total intensity observed for a set of overlapping reflections is apportioned among the reflections in the ratios of the calculated intensities (3,4). \( R_B \) is, therefore, biased in favor of the model being used. However, it is useful because it is relatively insensitive to features, such as profile shape errors, which produce an inflation of \( R_p \) and \( R_{wp} \) without crystal structural significance.
Cellotetraose is the $\beta$ 1,4-linked tetramer of D-glucose, $C_{24}H_{42}O_{21}$. Since the contributions of the hydrogen atoms to the x-ray pattern may be safely disregarded (Figure 3), structural determination consists of defining the x, y, and z coordinates (plus any thermal parameters) for each of the remaining 45 atoms in each tetramer. Even though 910 data points were taken, no more than about 30 intensity "peaks" can be observed, most of which are composites of several Bragg reflections. Therefore, only a very limited number of parameters in the model can be meaningfully refined.

The coordinates of the atoms in the monomer were assumed to be known from single crystal studies of glucose (7). Each monomer was treated as a rigid body with 3 degrees, each, of rotational and translational freedom.

The origin of the coordinate system (for example, coinciding with the center of the first monomer) can be freely chosen. The first monomer then has only 3 rotational degrees of freedom. The other three monomers are described by 3 translational and 3 angular parameters, each.

One parameter for each monomer describes the orientation of the oxygen of the primary hydroxyl group (O(6)), with respect to the C(4) - C(5) bond (see Figure 4 for the numbering of atoms).

With this selection of parameters, the tetramer is described in terms of 25 parameters. Specification of its orientation with respect to the unit cell requires another three angles. (In a strictly mathematical sense, these three parameters are redundant. Hence, they are never refined simultaneously with the orientation parameters of the monomers). Thus, the total number of parameters for the first tetramer is 28. It is then easy to describe many tetramers per unit cell; all one has to do is to take
28 parameters for the first tetramer and 28 parameters plus three for the additional translational degrees of freedom for each additional tetramer. For two tetramers this adds up to 59 parameters. In most of our refinements, the number of parameters actually refined in any one cycle was limited to about 20.

Only β-cellotetraose has been modeled in this study. The cellotetraose sample could also be a mixture of α- and β-cellotetraoses or even all α. In the case of mixtures, the anomers may occur in the same crystals as in the case of α-β maltose (8), or the powder sample may contain two types of similar crystals that differ at the anomeric carbon. This is among the topics that will be examined during the second phase of this study.

RESULTS AND DISCUSSION

Space Group and Unit cell parameters:

According to Poppleton and Mathieson (1), the space group for cellotetraose is either P1 or P2_1. The fairly strong 001 reflection observed at 3.90° (Figure 2) eliminates the P2_1 space group. Starting from those in the literature (2), the lattice parameters refined to

\[
\begin{align*}
\alpha &= 8.98 \, \text{Å}, \\
\beta &= 8.01 \, \text{Å}, \\
\gamma &= 22.34 \, \text{Å} \\
\alpha &= 94.31^\circ, \\
\beta &= 89.27^\circ \\
\gamma &= 116.45^\circ
\end{align*}
\]

These parameters agree well with the reported lattice parameters (2), except for \( \gamma \), which is smaller by 0.25 Å in our study. The density calculated from our parameters is 1.55 g/cm^3, that from (2) is 1.52 g/cm^3 and the measured density is reported (1) to be 1.49 g/cm^3.

The large, asymmetric (P1) unit cell permits 338 possible reflections in the angular range studied. Most peaks are composed of many unresolvable reflections. For instance, the major peaks at 12.3, 19.9, 22.0, and 40.8°
(to which 110, 110, 200, and 310, respectively, are the major contributors) contain 6, 9, 10 and 40 reflections, respectively. In the Rietveld method, the intensity at any point in the calculated diffraction pattern is the sum of contributions from neighboring reflections. In the diffraction patterns calculated in this work, the range of influence of any reflection was limited to twice the width of the profile at half the maximum height.

**Number of Tetramers per Unit Cell:**

**A: Trials with one tetramer per cell**

We first tried several models containing one tetramer per unit cell (of half the cell volume finally used), as proposed by Poppleton and Mathieson (1). However, we could not produce the roughly equal intensities of the two very strong peaks at 20 and 22° along with a strong one at 12°. We therefore concluded that the number of tetramers per unit cell is greater than one.

**B: Trials with two tetramers per cell**

As described by Gardner and Blackwell for cellulose (9), two tetramers can be packed in the unit cell in 3 ways: Parallel-up, antiparallel, and parallel-down. In parallel-up models, z-coordinates of the atoms at the reducing ends of both the tetramers are greater than those of the nonreducing ends, and conversely for the parallel-down models. Antiparallel models contain one "up" and one "down" tetramer. In their studies, Sarko and Muggli (10) have used a and the b axes which are interchanged compared to ours, those in the Blackwell-Gardner system, and those in references (1,2). This results in the c axis pointing in a direction opposite to that in the Blackwell-Gardner system. This has caused some confusion in that a parallel-up model in one system comes to be called a parallel-down model in the other system and vice versa.
We have refined several parallel-up and antiparallel models against the diffraction data and the best agreements between the calculated and the experimental data are shown in Figures 5 and 6. The ab and ac projections of the corresponding models are shown in Figures 7 and 8.

The R-values for the best models are given in Table 1. Since the R-values are fairly low (for x-ray Rietveld refinement), especially for the parallel up model, we believe that the general features of the models are correct. Before a final model can be proposed, however, factors such as the parallel down model, the O(6) position, the possibility of the α anomeric form, and the conformation angles between monomers in the tetramers must be more thoroughly examined. The cartesian and the fractional coordinates of the best available parallel-up and antiparallel models are given in Tables 2 and 3, respectively. In all the models, the molecular axes of the tetramers are slightly inclined with respect to the c axis.

O(6) position:

The position of O(6) is described by the conformation of the C(6)-O(6) bond with respect to the C(5)-O(5) and the C(4)-C(5) bonds. For example, if the C(6)-O(6) bond is trans to C(5)-O(5) and gauche to C(4)-C(5), then the position of O(6) is described as "tg".

The position of O(6) atoms in cellulose structures is at the center of several controversies. In an exploratory way, we have exploited the continuous dependence of the features of the powder diffraction pattern on crystal structural details to investigate the sensitivity of the diffraction pattern to changes in O(6) position. In the work reported in the following paragraphs, all Rwp values are for comparison of parallel-up models with the observed pattern. The position of O(6) was fixed as gg,tg,gt by specifying the torsion angle describing its position as 0.
120,120°, respectively). Also, the individual tetramers were close to having a 2-fold screw symmetry.

A. "tg" vs. "gt" models:

A powder diffraction pattern for a model with all O(6) atoms located in the "tg" position was calculated. \( R_{wp} \) was 0.20. This value is slightly higher than that of the best parallel model because in the best parallel model the O(6)'s are all positioned slightly away from "tg".

With all other parameters in the model kept unchanged, all the O(6) positions were changed to "gt". \( R_{wp} \) was 0.22, which indicates that the overall change in the pattern was small.

The calculated patterns for both the "tg" and the "gt" models are given in figure 9. The patterns are similar but a noticeable difference occurs in the peaks arising from the 004, 104 and 104 reflections (at 15.8°, 19.1° and at 19.6°, respectively). The sensitivity of the calculated pattern to changes in internal conformation, such as the O(6) position, makes it seem probable that a systematic study of the various O(6) positions and other internal changes will lead to lower \( R_{wp} \) values.

B. "tg" vs "tg, gt, tg, gt" models:

In the next model, the O(6) conformations were tg, gt, tg, gt (from the non-reducing to the reducing end). Again, the overall effect on the pattern was small (\( R_{wp} = 0.22 \)) but there were perceptible changes in non-zero "%" reflections (Figure 10), e.g., 002 has vanished. It is small but significant changes such as this that may ultimately lead to the correct model.

C."tg" vs "tg, gg, tg, gg" models:

Figure 11 shows that the very strong 110 and 200 reflections have changed considerably from the "tg" model. \( R_{wp} \) for this model was 0.25.

These computational experiments show that changes in the O(6) position
produce changes in the the reflections at small 2θ which are potentially analyzable even though the R_wp's for all of these models are fairly close.

Refinement of Parallel against Antiparallel Models:

In an attempt to learn how much information regarding chain polarity is available from powder diffraction data such as ours, we refined an antiparallel model against intensities calculated from a parallel model. Next, we refined the parallel model against the intensities calculated from that antiparallel model. The R_wp was only 14% in both cases. The similarity of these two calculated patterns (Figure 12) underlines the difficulty of choosing a model based on diffraction data alone. Spectroscopic data and hydrogen bonding possibilities should be useful making a final choice.

CONCLUSIONS

X-ray powder-diffraction data indicate that the unit cell for cellotetraose is triclinic (space group P1) with two tetramers per unit cell. Although there is a small preference for a parallel structure at this stage, similarities between patterns calculated for parallel and antiparallel models make it difficult to choose one over the other. In addition to the rather insensitive R values, the differences in specific reflections in the observed and the calculated patterns for different models may be used as criteria in selection of a model.

For fairly crystalline powders, such as cellotetraose, the Rietveld method seems to have a power comparable to fiber diffraction for typical cellulose samples. Peak overlap is even more severe, but the data are known with greater confidence because of less probable error in collection and correction of the data. Therefore, it is likely to be a worthwhile complement to the fiber method for highly crystalline samples, even if oriented samples are available.
Acknowledgements:

We thank Professor A.F. Turbak for helpful discussions and advice.

This material is based upon work supported in part by the U.S. Department of Agriculture under Co-operative Agreement No. 58-7b30-3-564.
BIBLIOGRAPHY

List of Tables

1. $R$ values for the best available models.

2. Fractional and cartesian coordinates of the best parallel model. Species 1 is oxygen and species 2 is carbon. The first 45 atoms are in the corner molecule and the next 45 atoms are in the center molecule. In each tetramer the first three monomers consist of 11 atoms each (6 carbon atoms and 5 oxygen atoms) and the monomer at the reducing end has 12 atoms (6 carbon atoms and 6 oxygen atoms).

3. Fractional and cartesian coordinates of the best anti-parallel model. Species 1 is oxygen and species 2 is carbon. The first 45 atoms are in the corner molecule and the next 45 atoms are in the center molecule. In each tetramer the first three monomers consist of 11 atoms each (6 carbon atoms and 5 oxygen atoms) and the monomer at the reducing end has 12 atoms (6 carbon atoms and 6 oxygen atoms).
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List of Figures

1. Wide angle x-ray powder diffraction pattern of cellotetraose at room temperature. Data were corrected for specimen transparency. CuKα radiation.

2. Small-angle powder-diffraction pattern of cellotetraose at room temperature (transmission mode). CuKα radiation and a position sensitive detector at 25.0 cm from the sample were used.

3. Calculated X-ray powder diffraction patterns for models with and without the hydrogen atoms. The pattern for the model not including hydrogen is shown by dots, the pattern for the model including hydrogen is shown in the same field, and their difference is shown in the lower field.


5. Calculated and observed patterns for the best parallel model. The observed pattern is shown by dots with vertical error bars based on counting statistics. The calculated pattern is shown by a continuous curve in the same field and the difference between the observed and the calculated patterns is shown in the lower field. Rwp for this model is 0.19.

6. Calculated and observed patterns for the best anti-parallel model. The observed pattern is shown by dots with vertical bars based on counting statistics. The calculated pattern is shown by a continuous curve in the same field and the difference between the observed and the calculated patterns is shown in the lower field. Rwp for this model is 0.226.

7. Best parallel model obtained from Rietveld refinement against observed pattern (Rwp =0.19). a) bc projection and b) ab projection. All the carbon and the oxygen atoms are shown for one corner and one central molecule only, in the unit cell. Only the oxygen atoms are shown for other
8. Best antiparallel model obtained from Rietveld refinement against observed pattern ($R_{wp} = 0.226$). a) bc projection b) ab projection. All the carbon and the oxygen atoms are shown for one corner and one central molecule only, in the unit cell. Only the oxygen atoms are shown for other molecules.

9. Calculated diffraction patterns with different C(6)-O(6) conformations. The pattern for the "tg" model is given by dots. The pattern for the "gt" model is given by the continuous curve. The difference is shown in the lower field.

10. Calculated diffraction patterns for models with different C(6)-O(6) conformations. The pattern for the "tg" model is given by dots. The pattern for the "tg,gt,tg,gt" model is given by the continuous curve. The difference is shown in the lower field.

11. Calculated diffraction patterns with different C(6)-O(6) conformations. The pattern for the "tg" model is given by dots. The pattern for the "tg,gg,tg,gg" model is given by the continuous curve in the same field. The difference is shown in the lower field.

12. Calculated diffraction patterns for parallel and antiparallel models refined against each other. The pattern for the parallel models is given by dots. The pattern for antiparallel model is given by the continuous curve in the same field. The difference is shown in the lower field.
Wide Angle X-ray Diffraction Pattern
Small Angle Diffraction Pattern

SCATTERING ANGLE

1.164 \times 10^4 \text{ COUNTS}
EFFECT OF INCLUDING H

1.555 x 10^4 COUNTS

SCATTERING ANGLE
PARALLEL UP,

1.596 X10^6 COUNTS

SCATTERING ANGLE
ANTIPARALLEL
TG VS GT

1.392 x 10^4 COUNTS

SCATTERING ANGLE
ALL TG VS TG, GG, TG, GG