MAGNETIC ANISOTROPY OF NATURALLY OCCURRING SUBSTANCES.

III. Wood and Its Constituents.

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Introduction.

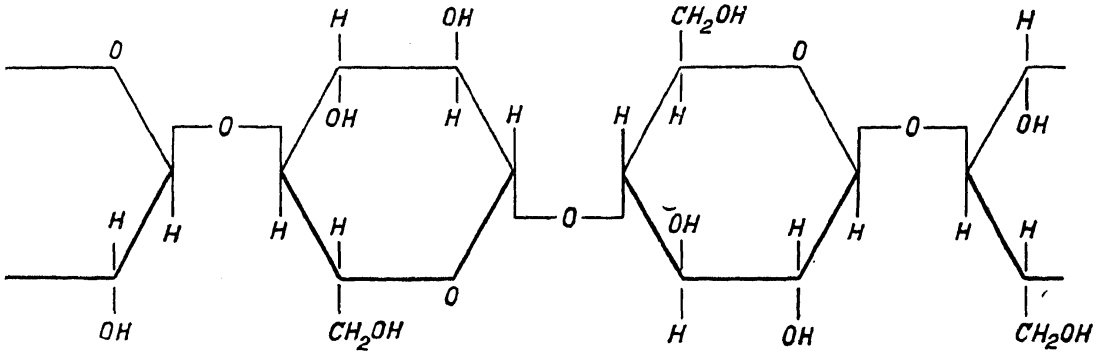
In previous communications[1] the author has shown how the study of the magnetic anisotropy of polycrystalline natural substances like mother of pearl enables us to obtain valuable information regarding the arrangement and orientation of anisotropic crystallites in the aggregate. In the light of the knowledge that we already possess concerning its structure and constitution, an extension of the magnetic studies to the case of wood should be expected to give results of considerable interest. Moreover, a knowledge of the magnetic properties of a universal substance like cellulose is still lacking although many of its other physical properties such as double-refraction, fluorescence, specific heat, hygroscopicity, thermal conductivity, elasticity, etc., have been investigated in greater or less detail. Wood cellulose, in view of the fact that it can be isolated from wood without serious damage to its intrinsic structure, is particularly suitable for the study of magnetic anisotropy. In the present paper the author has studied the absolute diamagnetic susceptibility and anisotropy of wood and its major constituents, with a view to gain additional information regarding their structure and to find out their directional magnetic properties.

The Structure and Constitution of Wood.

A knowledge of the structure of wood and its chemical constitution is essential for the interpretation of the magnetic data. The relevant facts are briefly mentioned in the following pages (for details see *Chemistry of Cellulose and Wood*, Schorger ; *Chemistry of Wood*, Hawley and Wise).[2]

The major constituents of wood are cellulose, lignin and the hemicelluloses. It is now known that cellulose is an ortho-glucosan, *i.e.*, glucose

anhydride. Its empirical formula is $(C_6H_{10}O_5)_n$. The molecule is made up of a chain of glucose residues linked by primary valence forces according to the following scheme :



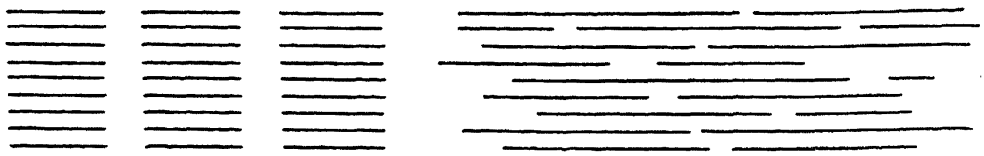
Fragment of Cellulose Chain.

FIG. 1.

Actually the unit in the cellulose chain is the cellobiose residue as will be seen from the arrangement of the glucose residues in the chain. It has been shown that all plant celluloses regardless of their source are identical. The cellulose in wood is found in the cell-wall of the tracheid and is 'crystalline'. With the fibre axis placed perpendicular to a beam of monochromatic X-rays, wood gives a fibre pattern characteristic of cellulose. An examination of teakwood by X-rays has been made by the author[3] and reported in a previous communication in which details regarding the character of the patterns and the information they yield about the structure of wood cellulose are given. The ' crystal structure ' of plant cellulose has been the subject of extensive investigations by Polanyi, Herzog, Sponsler and Dore, Astbury, Andress, Meyer and Mark, E. Sauter, Meyer and Misch and several others.[4] There is still considerable difference of opinion as regards the dimensions of the unit cell and atomic positions, and further investigation will be necessary to settle the question. But there is general agreement regarding the parallel orientation of the long chain molecules more or less in the direction of the fibre axis. Without laying special emphasis in the present uncertain character of the X-ray analysis, on the cell dimensions or the atomic parameters, we can definitely say that the length of the cellulose chain is parallel to the *b* axes of the 'crystallites' which possess monoclinic symmetry and are arranged spirally on the cell-wall (the spirals being steep enough to be almost straight in fibres like ramie and comparatively flat in cotton, wood, etc.) with the *b* axes orientated more or less along the spiral.

The character of the submicroscopic crystalline elements in cellulose is still in the course of being elucidated. Meyer and Mark at first came to the

conclusion from a critical examination of the available X-ray data that these were discrete micelles of dimensions 600 × 50 A. approximately. But it was shown later on that X-ray analysis can give no decisive answer to the question. On the basis of their physico-chemical investigations Staudinger[5] and his collaborators have favoured the view that the submicroscopic unit is the macro-molecule and not the micelle. A parallel arrangement of the macro-molecules bound together by secondary valence forces to form a bundle constitutes the cellulose lattice. The actual difference between the macro-molecular and the micellar schemes is brought out in the figure shown below.



Molecular Lattice. Macro-molecular Lattice.

FIG. 2.

But neither the macro-molecular nor the micellar theory has been able to account for the various physical and physico-chemical properties of cellulose satisfactorily. Recently, Frey-Wyssling, E. Sauter, Kratky and Mark and others[6] have attempted to arrive at a more rational hypothesis. Without entering into a detailed discussion of the various theories it may be said that the following incorporating the ideas of Frey-Wyssling and others is a fairly satisfactory picture of the internal architecture of the cell-wall in cellulose fibres. In the first place, we have the fibrils, running more or less along the fibre axis, which can be made visible under the microscope.[7] These consist of a parallel arrangement of the long-chain molecules of cellulose so placed that there are localised regions of perfect orientation (Kratky and Mark, 1937) which may be said to correspond to the crystalline micelles of the old theory, the forces between the molecules being of the Van der Vaals type in these regions. The dimensions of these micellar regions may be variable over a wide range, sometimes comprising the whole fibril. These ' crystallised ' regions are interspaced by either air cavities or by cementing matter like the pectins and the hemicelluloses. *The important fact to be noticed is that the regularity of arrangement of the cellulose chains in the fibre with their lengths parallel to the fibre axis should give rise to magnetic anisotropy if the individual molecules are themselves anisotropic and* vice versa, *the study of the magnetic anisotropy of wood cellulose should lead to a knowledge of the directional magnetic properties of the cellulose molecule.*

Lignin is present mostly in the primary layer of the cell-wall of the wood fibre known as the middle lamella. The constitution and the morphology of lignin have been the subjects of extensive investigations.[8] Examination by physical methods like microscopy, X-ray analysis and polarisation optics suggest that lignin is amorphous in structure. Various hypotheses have been put forward regarding the manner of combination of cellulose and lignin. One view is that they are chemically combined with each other, but the idea that lignin is adsorbed on cellulose seems to be more plausible in the light of the investigations by the physical methods mentioned above.

The hemi-celluloses[9] are the anhydrides of hexose and pentose sugars; xylan, araban, mannan and galactan give on hydrolysis xylose, arabinose, mannose and galactose respectively. Not much is known concerning their physical structure and manner of combination with cellulose and lignin.

Experimental Details.

The experiments were all confined to teakwood, the structure of which had been previously examined by the author by X-ray analysis. The wood specimens were subject to extractions with various solvents and subsequent chemical treatment in order to isolate the major constituents. The X-ray analysis was made incidentally to discover whether any radical structural changes had occurred during the extractions, etc. It was found that specimens taken from the less compact layers were subject to changes while those from the most compact layers were practically unaffected. The anisotropy measurements were therefore made on specimens obtained from the most compact dark brown layer of the annual rings. The specimens were prepared for examination as described below:

(1) *Raw wood.*—Washed clean with 5 per cent. HCl and warm water to remove surface impurities, and dried at 102–04° C. for 6 hours.

(2) Extracted with alcohol-benzene for 24 hours and then boiling water for 6 hours and finally dried for 12 hours at 102–04° C.

(3) Wood extracted as in (2) was treated with 5 per cent. NaOH in the cold for 48 hours. Washed several times with dilute acetic acid and then warm water and finally dried for 12 hours at 102–04° C.

(4) Treated with 72 per cent. sulphuric acid in the usual way for 36 hours to obtain lignin which retained the shape and continuous structure of the original sample of wood.

(5) Wood after extraction with alcohol-benzene was chlorinated by the Cross and Bevan method to obtain wood cellulose. The apparatus employed was similar to the one used by Sieber and Walter with a few minor modifications. The procedure described by Dore[10] was adopted with all the necessary precautions. Particular care was taken to see that the samples did not get distorted in shape during chlorination. The prepared samples were also subjected to X-ray analysis. Two samples of wood cellulose were prepared one by partial and the other by complete chlorination. The specimens were dried in the oven for 12 hours at 102–04° C.

(6) Wood cellulose was treated with 17·5 per cent. NaOH in order to get α-cellulose according to the procedure described by Schorger.[11]

Sampling of wood for magnetic measurements.—The wood samples were taken in the form of shavings about 0·5 mm. thick from which pieces 5 × 3 mm. were cut out for the anisotropy measurements. For measurements of absolute susceptibility the samples were taken in the form of powder.

Proximate Analysis of Wood.

The wood samples prepared as described before were all analysed for the determination of their cellulose and lignin contents. The hemi-celluloses and the rest were only indirectly estimated.

It must be stated beforehand that of all the various methods which have been suggested for the determination of the major constituents and groupings in wood, there is scarcely one which can be said to be entirely satisfactory. This, no doubt, is due to the inherent difficulties involved in dealing with a highly complicated substance like wood. The older methods for the determinations of cellulose, lignin and the hemi-celluloses have been continually refined, modified and standardised. However, for purposes of the magnetic investigation a high order of accuracy in analysis is not necessary, especially in view of the fact that the samples have to be taken in the form of shavings about 0·5 mm. thick for the anisotropy measurements, whereas the standard procedure in wood analysis is to start with saw-dust which passes through 80 but not 100 mesh. Therefore, the recent refinements and improvements in the estimation of lignin, etc., have not been adopted. The analytical procedure is outlined below and the results should be sufficiently accurate for interpreting the magnetic data.

Lignin.—The lignin content in the various samples was estimated by treatment with 72 per cent. sulphuric acid in the usual way.[12]

Cellulose.—Cellulose in wood was determined according to the analytical procedure described by Dore and already referred to earlier.

α-Cellulose in wood cellulose was also determined by treatment with cold 17·5 per cent. NaOH as described by Schorger.

Hemi-celluloses.—A direct determination of the hemi-cellulose content was not attempted. These were grouped with the small quantities of the other miscellaneous substances present and the whole indirectly estimated.

Determination of Magnetic Anisotropy.

The anisotropy of wood is comparatively feeble and the technique has to be made specially sensitive. The torsional method described by the author[13] in an earlier communication was employed with the following modifications : (1) Very fine and fairly long (20–30 cm.) quartz fibres were used. (2) The torsional constant of the fibre was determined by suspending at its end a small accurately cut-glass cylinder of known dimensions (3·15 mm. diameter and 4·01 mm. height) with its axis vertical and observing the period of oscillation. (3) A field strength of 7990 gauss was employed, the field being measured in the usual way by means of a calibrated Grassot Fluxmeter and search coil.

The specific anisotropy is given by the formula

$$\chi_1 - \chi_2 = \frac{2\,(\alpha_c - 45)\,\pi.\;c}{180 \qquad m\mathrm{H}^2}$$

α_c = The angle through which the torsion head has been rotated ;

m = Mass of the specimen (oven-dry sample) ;

H = Field strength in Gauss ; and

c = Modulus of torsion of the quartz fibre ;

and χ_1, χ_2 are the directions of maximum and minimum susceptibility algebraically in the plane of rotation of the specimen. Only $\chi_{\parallel^l} - \chi_{\perp^r}$ was found, since, in the case of wood, the anisotropy in the plane of the cross-section of the fibre is negligible in all cases. ($\chi_{\parallel^l}$ is the diamagnetic susceptibility along the fibre axis, and $\chi_{\perp^r}$ is that $\perp^r$ to the fibre axis.)

The average dimensions of the specimens employed were 5 × 3 × 0·5 mm.

Absolute Susceptibilities.

The absolute mass susceptibilities were determined by the Curie torsion balance method. The wood samples were all used in the form of fine powder dried at 102–04° C. for 12 hrs. and the susceptibilities compared with that of pure water.

Results.

Raw wood gave somewhat inconsistent values of anisotropy probably due to occluded impurities. After extraction with alcohol-benzene and boiling water consistent values were obtained, the maximum discrepancy noticed being 11 per cent. In all cases at least 10 independent determinations were made and the mean value taken. The results of the magnetic anisotropy measurements are given in Table I. Table II gives the values of absolute susceptibilities and Table III the results of the proximate analysis. A summary of results is given in Table IV.

TABLE I.

Specific Magnetic Anisotropy in C.G.S.—E.M. Units.

Specimen of wood	Mode of suspension	Orientation in the field	Specific magnetic antisotropy $-(\chi_{\parallel}i-\chi_{\perp}r)$, $\times 10^8$
(1) Extracted with alcohol benzene and boiling water	Fibre axis horizontal	Fibre axis perpendicular to the field direction	0·39
(2) After treatment with 5 per cent. NaOH	,,	,,	0·40
(3) Lignin prepared by treatment with 72% sulphuric acid	,,	nil	0·00
(4) (*a*) after partial chlorination,	,,	Fibre axis perpendicular to the field direction	0·68
(*b*) after complete chlorination	,,	,,	0·84
(5) α-Cellulose	,,	,,	0·92

TABLE II.

Absolute Mass Susceptibilities.

(C.G.S.—E.M. Units.)

Wood specimen	$-\chi \times 10^6$
(1) Teakwood : Most compact layer of annual ring	0·44
(2) ,, Least compact layer of annual ring	0·43
(3) ,, After extraction with alcohol-benzene and boiling water	0·47
(4) ,, After treatment with 5 per cent. NaOH ..	0·45
(5) ,, Lignin prepared by treatment with 72 per cent. sulphuric acid	0·42
(6) ,, After partial chlorination	0·48
(7) ,, After complete chlorination : Cross and Bevan cellulose	0·503
(8) ,, α-Cellulose	0·508

The diamagnetic susceptibility of pure double distilled water was taken as $-0{\cdot}720 \times 10^{-6}$.

TABLE III.

Proximate Analysis of Teakwood.

(Figures refer to percentage of oven-dry specimen taken.)

Specimen	Cellulose %	α-Cellulose %	Lignin %	Remaining hemi-cellulose, etc., indirectly estimated %
(1) Teakwood extracted with alcohol-benzene and water	54·1	39·9	33·5	12·4
(2) Treated with 5 per cent. NaOH	50·9	40·1	44·8	4·3
(3) After partial cholrination	82·8	59·3	14·7	2·5
(4) After complete chlorination : Cross and Bevan cellulose		72·9		

TABLE IV.

Summary of Results.

Wood specimen	Absolute susceptibility $-\chi \times 10^6$	Magnetic anisotropy $-(\chi_{\parallel}{}^{l}-\chi_{\perp}{}^{r})$, $\times 10^8$	Cellulose %	α-Cellulose %	Lignin %	Remaining hemi-celluloses, etc., %	$*\Delta\chi \times 100$ / % of total cellulose $\times 10^8$	$\Delta\chi \times 100$ / % of α-cellulose $\times 10^8$
After extraction with alcohol-benzene and boiling water	0·47	0·39	54	37	33	13	0·72	1·05
After extraction with 5 per cent. NaOH	0·45	0·40	51	40	45	4	0·78	1·00
Lignin prepared by treatment with 72 per cent. sulphuric acid	0·42	..	..	..	100	..	..	..
After partial chlorination	0·48	0·68	83	59	15	2	0·82	1·15
After complete chlorination: Cross and Bevan cellulose	0·503	0·84	100	73	..	..	0·84	1·16
α-Cellulose	0·508	0·92	..	100	..	..	..	0·92

$* \Delta\chi = -(\chi_{\parallel}{}^{l} - \chi_{\perp}{}^{r})$.

Discussion of Results.

An examination of Table IV shows that the anisotropy is more or less proportional to the cellulose content of the specimens. It apparently does not depend on the amount of lignin present. α-Cellulose has the maximum specific anisotropy whereas lignin isolated by 72 per cent. sulphuric acid treatment does not show any. The ' crystalline ' element responsible for the magnetic anisotropy appears to be cellulose only.

The magnetic measurements, however, do not rule out the possibility of lignin being present as crystallites which are randomly orientated. But X-ray analysis shows that isolated lignin gives only a ' liquid ' pattern characteristic of an amorphous substance.[14] There is also nothing indicative of ' crystalline ' lignin in the wood patterns obtained. Examination of lignin under the microscope has not revealed any property characteristic of crystals, due to it. Taken together, the X-ray, optical and magnetic investigations lead to the conclusion that lignin in its natural state has an amorphous structure.

Ordinary wood cellulose obtained by chlorination is really a complex substance and consists of what are known as the α, β and γ-celluloses, distinguished from one another by their solubility in 17·5 per cent. NaOH solution. From Table IV we can see that the magnetic anisotropy of wood is essentially due to the α-cellulose in it. It is also seen that treatment with 5 per cent. NaOH which removes a good part of the hemi-celluloses leads to an increase in the value of $\frac{\Delta\chi}{\%\text{ of total cellulose}}$. The initial removal of the hemi-celluloses naturally means a decrease in the total cellulose, for wood cellulose (prepared without pre-treatment with NaOH) contains as much as 20 per cent of the hemi-celluloses. We may conclude from this that the hemi-celluloses like lignin do not contribute to the magnetic anisotropy. In view of their gummy texture it is most probable that they are amorphous in structure.

We also notice that the value of $\frac{\Delta\chi}{\%\text{ of }\alpha\text{-cellulose}}$ is less for α-cellulose than for Cross and Bevan cellulose. This will mean that $\Delta\chi$ is greater for Cross and Bevan cellulose than can be accounted for by the presence of α-cellulose alone in it. The inference is that the β- and γ-celluloses are also anisotropic just like α-cellulose and most probably possess the same ' crystalline ' structure.

Magnetic properties of the cellulose molecule.—The diamagnetic anisotropy of cellulose in wood leads to important conclusions regarding the

directional magnetic properties of the cellulose molecule. The diamagnetic susceptibility in the direction of the fibre axis is seen to be maximum. Since the cellulose chains are orientated with their lengths more or less parallel to the fibre axis it follows that the direction of maximum diamagnetic susceptibility is along the chain length. The values of $\chi_{\parallel}{}^{l}$ and $\chi_{\perp}{}^{r}$ can be easily calculated from $\bar{\chi}$ and $\Delta\chi$. We have $\chi_{\parallel}{}^{l} = -0{\cdot}514 \times 10^{-6}$ and $\chi_{\perp}{}^{r} = -0{\cdot}505 \times 10^{-6}$, for α-cellulose.

Now, it is well known from the data of refraction of cellulose[15] that the direction of maximum optical polarisability of the cellulose molecule is also along the length of the chain. The directions of maximum optical polarisability and diamagnetic susceptibility, therefore, coincide. This, in fact, is not surprising since this property is also possessed by long-chain aliphatic compounds like the higher hydrocarbons (C_nH_{2n+2}).[16] By analogy we can also draw the inference that a solution of native cellulose in neutral solvent will exhibit negative magnetic double refraction, in accordance with the orientation theory of Langevin and Born.

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Summary.

The diamagnetic anisotropy and absolute susceptibilities of wood, lignin and wood cellulose have been determined. It has been found that the 'crystalline' element in wood is definitely cellulose and that lignin and the hemi-celluloses make no contribution to the magnetic anisotropy, suggesting either a random orientation if they are crystalline or an amorphous structure. In the light of evidence from other sources, it seems most likely that they are amorphous. The anisotropy measurements also indicate that the direction of maximum diamagnetic susceptibility in the cellulose molecule is along the length of the chain. Since it is also known that the direction of maximum electric polarisability too is along the chain length, we find that these directions coincide in the molecule just as in the case of the higher long-chain saturated hydrocarbons.

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