X-RAY STUDIES OF WOOD, LIGNIN AND WOOD-CELLULOSE.

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Introduction.

The investigation of wood by X-rays is still in its infancy but the results already obtained bid fair to be of considerable importance. Till now only a few European woods like elm, ash, pine, oak, etc., have been studied in any great detail.[1] The study of Indian woods by X-ray analysis offers a field of immense interest, and in the present paper the author has commenced such a study. A general scheme of examination of wood divides itself naturally into two parts; firstly, the exhaustive study of some typical woods and secondly, a comparative study of the various woods in relation to their structural properties. The Indian teak, on account of its abundance in India and great practical importance, has been first taken up for investigation.

Teak (*Tectona grandis*) is found in India, Burmah, Ceylon, the Malay Peninsula and the East Indies. The tree grows to a height of 80–100 ft. and the trunk is 3–4 ft. in diameter in full-grown trees. The colour of the wood varies from yellow to brown. The grain is straight and even. The annual rings in the heartwood are of unequal thickness varying from about 2 mm. to 10 mm. Each ring consists of an outer brown compact layer and an inner layer of lighter tint which is less compact. The transition from the one layer to the other in the same annual ring is not sharp as in some of the European woods like oak or pine. The annual rings are, however, very well defined.

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[1] R. O. Herzog and W. Jancke, *Ber.*, 1920, **53**, 2163.
K. Weissenberg, *Z. Phys.*, 1921, **8**, 20.
S. Pienkowski, *Z. Phys.*, 1930, **63**, 610.
B. Schmidt, *Z. Phys.*, 1931, **71**, 696.
G. L. Clark, *Applied X-rays.*
K. Freudenberg, *Pap. Fab.* 30. *Tech. Wiss. teil.*, 1932, **189**, 97.
R. D. Preston, *Phil. Trans.*, (B), 1935, **224**, 131.
E. M. Miles Thomson and J. Hewitt, *Nature*, 1935, **136**, 69-70.

It is well known that wood gives an X-ray pattern more or less identical with that obtained from fibres like cotton, ramie, etc., thereby showing that the cellulose in wood is of the same crystalline character. It has also been noticed by earlier workers in the field that often the orientation of the cellulose micelles is far from perfect in wood.* This has been attributed to a spiral arrangement of the micelles in the fibre.[2]

The following aspects of the problem have been investigated :—

(1) The effect of extraction with different solvents and chemical treatment on wood-structure. This besides being of interest to the wood chemist has a speical significance in connection with the study of the magnetic anisotropy of wood which the author has undertaken. More will be said about this later.

(2) Study of wood-cellulose and lignin, isolated by standard methods.

(3) Comparative study of the different layers in a healthy annual ring from the heartwood.

(4) The effect of swelling.

Experimental Details.

A fine-structure-examination tube made by R. Seifert and Co., Hamburg, was used, the anticathode being of copper. The applied voltage across the tube was 40 KV. and the tube current was kept at 15 m.A. Exposures of $2\frac{1}{2}$ hours were given where not specified otherwise. The dimensions of the specimens ranged from 0·5 to 0·8 mm. in thickness and about 5 mm. in length.

In order to study the effect of extraction with various solvents and chemical treatment, the general procedure of the wood analyst was adopted in the preparation of the specimens.[3] Though the sampling of wood in respect of size is important in analysis, it is not a decisive factor in this connection. However, the periods of extraction were prolonged and the method modified where necessary, in view of the comparatively larger size of the samples employed. The specimens were all taken from the middle layer of an annual ring 8 mm. in thickness from a healthy even-grained

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* The micellar crystallite theory of cellulose structure favoured by Meyer and Mark has been adopted in the present paper as a working hypothesis, although there is difference of opinion on this point.

[2] K. Weissenberg, *loc. cit.*
Steinbrinck, *C. biol. Zbl.*, 1925, **45**, 15.

[3] Hawley and Wise, *The Chemistry of Wood ; The Chemical Catalogue Co.*, 1926.
Schorger, *Chemistry of Cellulose and Wood*, McGraw-Hill Book Co., 1926.

part of the heartwood. They were subjected to the following treatments in succession and the X-ray pattern taken at each stage :—

(*a*) Specimen as such dried at 102°C. for 6 hrs.

(*b*) Extracted with alcohol-benzene for 12 hrs.; then washed and extracted with boiling water for 2 hrs. and finally washed and dried at 102°C. for 6 hrs.

(*c*) Sample (*b*) was then extracted with 1 per cent. KOH for 2 hrs. in a flask with reflux condenser, washed with warm water, treated with 1 per cent. acetic acid, finally washed with warm water and dried at 102°C. for 6 hrs.

(*d*) After the above extractions the sample was chlorinated by the Cross and Bevan method with an apparatus similar to that of Sieiber and Walter.[4] The wood-cellulose was thoroughly washed with hot water and dried at 102°C. for 6 hrs. Great care was taken in the manipulation so that the specimens did not get distorted. It was possible to get excellent white celloulse which retained perfectly the shape of the original specimen of wood.

The X-ray patterns were all taken with the tangential sections of the wood-specimen perpendicular to the incident X-ray beam, where not specified otherwise. The distance from the specimen to the film was 5·01 cm.

Lignin was prepared by Ritter's method.[5] Ritter has separated two types of lignin by treatment of wood with 72 per cent. H_2SO_4; one is the 'amorphous' lignin which separates out from the bulk and the other is that which retains a continuous structure and the shape of the original wood-specimen. The dimensions of the pieces used for extraction were $1 \times 2 \times 5$ mm. After washing, and drying at 102°C. samples 1 mm. in thickness were cut out from the bigger pieces.

For the study of swelling the following arrangement was adopted. The specimen taken from the compact layer of an annual ring 8 mm. thick after being soaked in water for 36 hrs., was fixed in the middle of a cup-like hollow made of soft wax, about 4 mm. deep. The cup was filled with water so that the specimen is throughout the duration of the exposure saturated with water. The X-ray beam is incident on the part of the specimen projecting above the water level. Two patterns were obtained, one on each half of the same film, with the dry specimen and with the specimen soaked in water, respectively. The complete X-ray diagram of soaked wood was also taken separately for purposes of measurement.

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[4] See Dore, *Ind. Eng. Chem.*, 1920, 12, 264.

[5] Ritter, *Ind. Eng. Chem.*, 1925, 17, 1194.

The mean results of a partial analysis of three samples of heartwood (in the form of powder passing 60- but not 100-mesh sieve) are as follows :—

Ash	0·47 %
Alcohol-Benzene and boiling water soluble portion	13·1 %
Lignin	27·3 %
Cellulose	47·9 %

The determinations were made on oven-dry sample. Lignin was estimated by the sulphuric acid method. For cellulose determination, the procedure recommended by Dore was adopted, the sample being extracted with alcoholbenzene and hot water before chlorination.

Discussion.

Chemical treatment can affect wood-structure in two ways : (1) it can bring about a change of micellar orientation in the fibres and (2) it can cause a modification of the crystal lattice due to the formation of some cellulose derivative (we do not consider here these changes which radically alter the cellulose structure). A familiar instance of the change brought about in the lattice spacing is the formation of hydrate-cellulose when native cellulose is treated with fairly concentrated alkali.[6] It is well known that a perfect fibre pattern corresponds to the rotation pattern of a single crystal, the spots being sharp and distinct. When there is defective orientation with respect to the fibre-axis the spots are drawn out into arcs, and in the case of complete dis-orientation the arcs become rings. The X-ray diagrams (*a*), (*b*), (*c*) and (*d*) are those of untreated wood, wood extracted with alcohol-benzene and boiling water, wood extracted with alcohol-benzene and boiling water followed by 1 per cent. KOH, and chlorinated wood (Cross and Bevan cellulose) respectively.

On examination of the patterns it was found that no detectable changes in the lattice had taken place. This is an indication that the cellulose remains unaffected throughout, as regards its crystalline character.

The following points were, however, noted :—

(1) Variation in the relative orientation of the micelles takes place at each stage of extraction or chemical treatment.

(2) There is a progressive decrease in the background scattering after each stage of extraction or chemical treatment.

(3) The pattern of wood-cellulose is less intense than that of wood.

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[6] K. H. Meyer aud H. Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Leipzig, 1930.

The change in the error of orientation of the micelles is significant. After the alcohol-benzene extraction the pattern becomes distinctly sharper indicating a better alignment of the cellulose micelles parallel to the fibre axis. There is also a slight increase in the sharpness after treatment with 1 per cent. KOH but on chlorination we again notice a dis-array setting in. This can be easily accounted for. The lignin in the middle lamella has been removed during chlorination creating spaces in which the micelles, can get slightly displaced and disoriented.

The work of K. Kanamaru[7] on the double-refraction of native cellulose, is noteworthy in this connection. He experimented with the fibres of ramie, hemp, jute, bamboo and straw. These were extracted successively with alcohol-benzene, boiling water, 1 per cent. NaOH, and finally chlorinated by the Cross and Bevan method. The orientation-angle of the micelles could be calculated from the data of double-refraction employing an elliptic equation given by Frey.[8] For the birefringence of cellulose is due to the regular arrangement of anisotropic crystallites in the fibre, and when there is a change in the orientation of the crystallites there will be a corresponding change in the double-refraction also. K. Kanamaru has found that in the case of ramie and hemp the regularity of arrangement increases after each stage of extraction while in the case of highly lignified fibres like jute, bamboo and straw, there is a marked decrease in the angle of dis-orientation after extraction with alcohol-benzene, water, and 1 per cent. NaOH followed by an increase on chlorination. There seems to be qualitative agreement between the results obtained by Kanamaru for highly lignified fibres and those obtained by the author for wood by X-ray analysis. From the X-ray diagrams the approximate angle of dis-orientation can be estimated. These come out to be (*a*) 30°, (*b*) 20°, (*c*) 15°, and (*d*) 25°, respectively. These may be compared with the angles calculated by Kanamaru for jute, 32°, 25°, 5°, and 23° respectively, from the data of double-refraction.

The decrease in the background scattering is evidently due to the removal of the amorphous scattering matter during the successive stages of extraction and chemical treatment.

The patterns also suggest that the dimensions of the cellulose micelles are of the same order of magnitude as found by Hengstenberg and Mark[9] in ramie.

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[7] K. Kanamaru, *Hel. Chim. Acta*, 1934, **17**, 1017-66.
[8] A. Frey, *Koll. Chem. beihefte*, 1927, **23**, 48-49.
[9] J. Hengstenberg and H. Mark, *Zeit. f. Krist.*, 1928, **69**, 271.

There seems to be nothing characteristic of lignin in the patterns except the diffuse scattering. This confirms the amorphous character of lignin, a fact which has also been recognised by earlier workers. As a further confirmation, the author has obtained the X-ray interference diagram of Ritter's lignin, Figs. (*e*) and (*f*). This closely resembles that of an amorphous substance like bituminous coal. In (*e*), time of exposure 4 hrs., it was just possible to make out a diffraction maximum on the film corresponding to a Bragg spacing of 4·3 A. (*f*) was obtained after 6 hrs. exposure and the diffuse scattering was sufficiently intense to mask the halo. *If we assume that the changes brought about in the lignin-structure during the chemical isolation are not of a very drastic character* in view of the fact that the lignin retains the continuous structure and the shape of the original specimen of wood, then it may be inferred that lignin is definitely amorphous.

Comparison of Figs. (*g*), (*a*) and (*h*) is very revealing. Fig. (*g*) is the pattern due to the brown compact layer of an annual ring 8 mm. in thickness from the heart-wood, (*a*) is that of the middle layer, and (*h*) of the ochre-coloured layer where the hollow tubular canals are most prominent. The first is a spot pattern indicating almost perfect orientation of the micelles. In (*a*) the spots are seen to be drawn out into arcs, which means a slight error in the micellar orientation, while in (*h*) we have almost a ring pattern. A ring pattern here might imply, (1) a completely random arrangement of the micelles in the fibres, the fibres themselves being perfectly parallel to each other, (2) perfect orientation of the micelles in the fibres, but a haphazard arrangement of the fibres, or (3) both disorderly arrangement of the fibres as well as a large error in the orientation of the crystallites in the fibre. By examination under the microscope it was observed that in the less compact yellow layer the fibres were not placed quite parallel to each other, largely on account of the presence of the tubular canals. This by itself cannot, however, explain the ring pattern. We are led to conclude that there is also considerable dis-orientation of the cellulose micelles in the fibres in this layer.

It is evident therefore that *as we proceed from the most compact towards the least compact layers in an annual ring there is progressive dis-orientation of the cellulose micelles in the fibre with respect to the fibre-axis.* We also find that in the most compact layers of wood the micellar orientation can be as perfect as in ramie. If the apparent dis-array of the micelles is due to a spiral arrangement, as has been proposed, then it may be inferred that the micellar spiral is flat in the one case and steep in the other.

S. Pienkowski and B. Schmidt have obtained similar results in the case of European woods like ash, elm, fir, etc.[10] Compact layers (springwood or summerwood as the case may be) showed good orientation of the crystallites whereas the less compact layers showed pronounced dis-orientation. E. M. Miles Thomson and J. Hewitt have also reported an almost perfect micellar orientation in the case of oak, but their investigation is less complete.[11] The latter authors have not mentioned from which part of the annual ring their specimen was taken. This is, however, very important as shown by the results obtained by S. Pienkowski, B. Schmidt and the author in the present paper.

It may be pointed out here that very often the workers in the field do not give the full botanical names of the woods they have investigated. By the mere designation such as pine, fir, or ash there is room for confusion. There are several species of these trees, in some of which the wood is hard and in others soft. For instance we have the soft pines and the hard pines, the structural properties of which are very different. For any comparative study of the different woods by X-ray analysis in relation to their structural and other properties, it is essential to know details such as the species of the tree, its locality of growth, nature of the wood, etc.

In Fig. (*i*) we have the patterns of dry wood and wood saturated with water respectively, taken on each half of the same film. The swelling of wood is a highly interesting phenomenon. The pressures developed when wood swells are so enormous that even rocks can be split. Swelling has been studied by Katz, Hess and others in great detail.[12] Katz describes the swelling of native cellulose as intermicellar since no essential difference could be observed in the X-ray interference diagram after swelling. In Fig. (*i*) we see that the diffuse scattering is more pronounced in the pattern of swollen wood. The complete pattern also was taken on a separate film and measured. No perceptible change could be observed in either the relative positions or the intensities of the spots.* A slight equatorial broadening of the spots could be noticed, obviously due to the slight increase in the thickness of the specimen on swelling. The water bands did not appear. There is also no perceptible change of micellar orientation. The swelling of wood is evidently an intermicellar phenomenon. Recently a case of intramicellar swelling of cellulose has been reported by

[10] S. Pienkowski, *loc. cit.*
B. Schmidt, *loc. cit.*

[11] E. M. Miles Thomson and J. Hewitt, *loc. cit.*

[12] J. R. Katz, *Trans. Far. Soc.*, 1933, **29**, 279-97, is a resume of the work done on swelling.

* See G. L. Clark, *Ind. Eng. Chem.*, 1930, **22**, 482.

I. Sakurada and K. Hutino,[13] but here the swelling is brought about in a different manner.

Fig. (*j*) is the pattern of the woody layer in the region of a knot, showing a large error in the micellar orientation.

Patterns (*k*) and (*l*) are those of a wood-specimen placed with the tangential and radial sections respectively perpendicular to the X-ray beam. It can be easily seen that (*k*) is a much sharper pattern than (*l*). On examining the specimen under the microscope it was observed that the parallel arrangement of the tracheids was more perfect in the tangential section. This would account for the relative sharpness of the spots in the one case and the diffuseness in the other. This would also explain why teakwood can be split in the radial section with greater ease.

The patterns for the springwood of fir, and the summerwood of ash, obtained by B. Schmidt bear a close resemblance to that of the compact layer in teakwood, Fig. (*g*). This would indicate that there is no essential difference in the orientation of the micelles in the fibre in the compact layers of the coniferous trees (Gymnosperms) and the broad-leaf trees (Angiosperms).

It has been mentioned earlier that the study of the effect of chemical treatment on wood-structure by X-rays has a special significance in connection with its magnetic anisotropy. The author found that wood *as such* gave quite inconsistent values of magnetic anisotropy. This was attributed to the presence of miscellaneous matter and the procedure of the wood analyst was adopted to remove these and ultimately obtain wood-cellulose. After the alcohol-benzene extraction the values became remarkably consistent. The specific anisotropy was found to increase after each stage of extraction. The X-ray studies were made in order to ascertain whether any change of structure or micellar arrangement had taken place, and if so to find out the exact nature of the change. The magnetic investigation is not yet complete but the results obtained clearly indicate that the crystalline element in wood is cellulose and that lignin *as it is present in wood* is amorphous. The details will be published later.

In conclusion, I wish to express my sincere thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work and valuable criticism. My thanks are also due to Dr. S. Rama Swamy for help given when taking the X-ray photographs.

[13] I. Sakurada and K. Hutino, *Koll. Zeits.*, 1936, 77, 3, 346.

Summary.

The structure of teakwood has been examined by means of X-rays. It has been found that in the annual ring of the heartwood there is almost perfect micellar orientation with respect to the fibre-axis in the brown compact layer, while in the less compact layers there is a relatively large error of orientation. In fact, as we proceed from the most compact towards the least compact layer in the annual ring, there is progressive dis-orientation of the micelles in the fibre. Extraction of wood with various solvents, and chemical treatment, are found to affect the disposition of the micelles relative to the fibre-axis to a marked extent, and these changes have been studied. It has been confirmed that when wood swells in water there is no change of crystal lattice; the phenomenon is intermicellar. Wood-structure near the region of knots and the structurel differences along tangential and radial directions have also been investigated.