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THE ELASTIC ANISOTROPY OF KERATINOUS SOLIDS

I. THE DILATATIONAL ELASTIC CONSTANTS

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Summary

The elastic anisotropy of four forms of α -keratin, ram's horn, rhinoceros horn, baleen (whalebone), and the cortex of African porcupine quill, has been studied by measurement of the velocity of propagation of dilatational elastic waves of 5 Mc/s frequency along the principal axes, by the total reflection method. It has been found that ram's horn is transversely isotropic about the radial direction and that rhinoceros horn is approximately transversely isotropic about the fibre direction. This is directly correlated with the histological structure of these materials, which here predominates over the molecular structure in determining the nature of the elastic anisotropy.

All three principal velocities and the corresponding elastic constants have been determined for ram's horn and rhinoceros horn, and two of them for baleen. Some less accurate data are presented for two of the principal directions in African porcupine quill cortex. For ram's horn the approximate values of the elastic constants which govern the propagation of dilatational waves along and perpendicular to the radial direction are 0.85 and 1.01×10^{11} dyn cm⁻² respectively; for rhinoceros horn perpendicular and parallel to the direction of growth, 0.84 and 1.09×10^{11} dyn cm⁻².

I. INTRODUCTION

Owing to the complexity of the molecular structure of keratin and to the inhomogeneity of the available keratinous materials, the molecular structure cannot be determined completely from X-ray diffraction data alone. Other data have also to be considered; among these, the viscoelastic properties are important.

Except in a few cases (e.g. Warburton 1948; MacArthur 1943) the elastic properties of α -keratin have been studied only for keratin in the form of fibres; the obvious limitations of both the interpretation and the technique of transverse measurements have confined such studies to extension or contraction along the fibre axis and torsion about this axis. The high extensibility along the axis has been used by Astbury and many later workers as a basis for the postulation of the various folded chain structures of α -keratin. Fruitful as this concept has been, the validity, in general, of the direct attribution to the molecule of the total elastic behaviour of an anisotropic, inhomogeneous keratin fibre, with its well-defined histological structure, cannot be regarded as firmly established. If a complete study were made of the anisotropy of various forms

of keratin over a wide range of strains and frequencies, it might be possible to separate that component of the elastic behaviour which is due to the molecules of crystalline keratin from those components which are due to the histological structure and to the disordered regions. In the range of very small strains, determination of all the principal elastic constants of different forms of keratin might provide data which could be used as a test of proposed molecular structures. Even an incomplete study could test the relative importance of the molecular and the histological structures in determining the elastic behaviour.

The data obtained would be useful in other problems also, such as that of the absorption of water by keratin (cf. Cassie 1945).

A complete study will obviously be very lengthy, and will have to be carried out gradually. A beginning has been made in the work to be described in this and a subsequent paper.

II. EXPERIMENTAL METHOD

The experimental technique used has been described elsewhere (Makinson 1952) in its application to isotropic solids, and will only be outlined here. A thin, acute-angled wedge of the solid is immersed vertically in oil in the path of a horizontal ultrasonic beam of frequency 5 Mc/s. The beam transmitted through the wedge is observed by the diffraction which it produces in a perpendicular beam of light. The angle of incidence ϕ' is measured at which certain characteristic zeros of transmission occur for several different regions along the wedge. This angle is the critical angle of total reflection of the dilatational (or longitudinal) elastic wave, which is then propagating in the solid parallel to the width of the wedge, i.e. $\phi' = \sin^{-1} \omega_d / \omega_0$, where ω_0 is the velocity of the ultrasonic wave in the oil and ω_d is the velocity of the dilatational wave in the solid. Hence ω_d is calculated. The corresponding elastic constant is equal to $\rho \omega_d^2$, where ρ is the density of the solid. It is greater than the Young's modulus of the solid (see Section VI).

The ultrasonic power used is very low, so that all strains in the solid are very small and lie in the elastic region.

The method is not in general applicable to an anisotropic solid, since in this case there is in general no purely dilatational refracted wave. It is applicable if (i) the crystallographic axes of the solid are mutually perpendicular, and (ii) the principal directions of the wedge lie along these axes. The method was applicable, either exactly or to a close approximation, to all the specimens studied in the main line of this work.

Following usual crystallographic practice, as summarized by Hearmon (1946), the dilatational elastic constant in the i direction is written c_{ii} , e.g. the elastic constants governing the propagation of dilatational waves in the r , θ , and z directions are written c_{rr} , $c_{\theta\theta}$, and c_{zz} .

There are practical difficulties in applying the method to keratinous solids, since the available specimens of keratin are inhomogeneous, of inconvenient shapes, and of limited sizes. It was not always possible to cut sufficiently large

and well-oriented wedges in all the directions necessary for the determination of all three of the constants c_{ii} , so that some of the data are incomplete. Nevertheless, it was possible to draw some unambiguous conclusions from the measurements.

In the cortex of ram's horn regions of slightly different densities were found to occur. The density was determined with respect to the oil which surrounded the specimens. The values for the wedges used fell into two groups, around 1.28 and 1.31 g cm⁻³, the difference being greater than the experimental error. The grouping did not correspond to particular orientations of the wedges, so that the lower densities are unlikely to have been due to such effects as penetration of air along the grain. It was impossible to avoid altogether the use of the material of lower density. However, the results obtained showed no correlation between this density variation and the measured velocity, whereas there was complete correlation between the direction of propagation and the velocity. In calculation of the elastic moduli c_{ii} for horn, the actual density relative to the oil for each specimen has been used, but only about 2 per cent. change would have been made in any value of the moduli by using a mean value of the density, and this would not have affected the main conclusions.

A less thorough study of density variations was made for the other materials used. The range for rhinoceros horn was 1.29 to 1.31, the value for the outer layer of baleen was 1.29, and that for the side wall of porcupine quill, after it had been boiled under moderate pressure to flatten it, was 1.32.

The regain of the keratin was not closely controlled, nor was the temperature of the measurements. It has been found by other workers (Chaikin 1953) and was confirmed by the results described here, that at frequencies in the megacycle range the elastic constants are much less sensitive to regain and temperature than at low frequencies. The specimens were stored and used in a room in which the day temperature varied from about 17.5° to about 22°C, being usually near 20°C, and the day humidity varied from about 35 to 60 per cent. For measurement, the specimens were immersed in a 4-gal tank of technical white oil which over a period of a year or more had come to equilibrium with the average moisture content of the air in the room. No dependence of the measurements on the room conditions was observed.

III. PREPARATION OF THE SPECIMENS

The materials used were ram's horn, rhinoceros horn, and baleen (whale-bone) from a rorqual. A few data which were of only qualitative value were obtained with African porcupine quill. In general, plates as large as possible up to about 8 by 4 by 0.5 cm were cut at the required orientation from the cortex of the various materials, and were formed into wedges of from 0.12 to 2.0 mm thickness by cementing each side in turn to a steel template with celluloid cement and shaping them with a shaper (milling and sanding were found to be unsatisfactory techniques). The wedges were then released from the template with amyl acetate and washed in the same liquid. For the baleen the outer layer, or "cut," was used. For porcupine quill (a) plates were made

by cementing together a number of pieces of tip; (b) cylindrical pieces of quill cortex were flattened out in boiling water, as described by Rudall (1936). This treatment, of course, may have changed the structure of the quill. Neither process gave satisfactory specimens, and the data obtained are of only qualitative value.

The nomenclature adopted for the crystallographic axes, in the ram's horn, baleen, and porcupine quill, was: z axis, the direction of growth, i.e. the "fibre" direction; r axis, the radial or thickness direction; θ axis, the circumferential or width direction. These were rectilinear Cartesian, not polar axes, since the ram's horn had an approximately triangular section, from which flat wedges could be cut, the baleen was naturally flat, and the porcupine quill was used flattened out. In rhinoceros horn the principal directions were taken as: z axis, direction of growth (fibre direction); l axis, direction of major (long) diameter of cross section; s axis, direction of minor (short) diameter of cross section.

The relation of these directions to the structure of the materials will be made clearer in Section V.

Owing to the spiral growth of ram's horn, the direction of the z axis varied along the wedge. The straightest portions were used as far as possible, and the misalignment was usually not greater than 4.5° at the important parts of the wedges. It was found that the measured velocity was not very sensitive to this error, owing partly to the low anisotropy of ram's horn.

IV. EXPERIMENTAL RESULTS

The values of the elastic constants are shown in Figure 1 and Table 1, and the wave velocities are also given in Table 1. Some comments are necessary on the estimation of the errors. The specimens I to XI of ram's horn were all different wedges, and for any set of specimens in which the width of the wedge, i.e. the direction of propagation of the dilatational wave, lay along one crystallographic axis (e.g. r), some of the specimens had their length along the second crystallographic axis (e.g. θ) and others had their length along the third axis (e.g. z). For each of the specimens except V, VIII, X, and XI the wedge was long enough to permit the observation of two series of transmission zeros (these were not always the first and second series described previously (Makinson 1952)). The two values for XI both refer to the same series. As has been shown previously (Makinson 1952) there is a small systematic discrepancy between the values of ϕ' for different series of zeros. Also, the distribution of points in any one series is not usually Gaussian but shows a definite trend with thickness of the wedge, and for some orientations of the crystallographic axes the zeros are wider than for others. Generous estimates have therefore been made of the errors for each series of zeros by taking as "likely error" that corresponding to the extreme angular range of the centres of the zeros in each series, and as "extreme possible error" that corresponding to the extreme angular range over which zeros of transmission extend. This latter almost certainly considerably over-estimates the error for any one set of measurements.

The specimens of rhinoceros horn sub-indexed (*b*) and (*c*) were made from the corresponding (*a*) by machining it thinner. This shifted the positions of the minima along the wedges, so that a different part could be studied. These wedges were longer than those of ram's horn, so that it was sometimes possible to obtain three series of zeros. All the values given for any one specimen refer to different series.

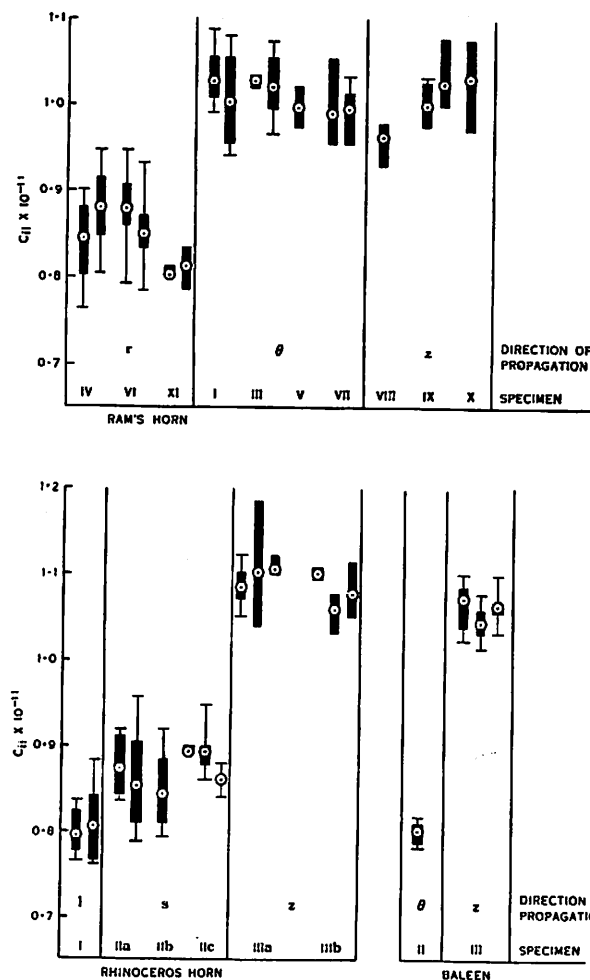


Fig. 1.—Dilatational elastic constants c_{ii} of some forms of α -keratin: Broad line indicates "likely error" and thin line "extreme possible error" (see text).

It must be remembered that there will also be variations in the measured moduli arising from true variability of the keratinous materials.

The data of Table 1 and Figure 1 show that ram's horn is transversely isotropic about r (i.e. the elastic behaviour is the same in all directions perpen-

dicular to r), whereas rhinoceros horn is approximately transversely isotropic about z ; rhinoceros horn may in fact be orthorhombic, but the difference between the r and s directions is barely significant. For baleen and for porcupine quill, owing to their thinness in the r direction, data could be obtained only in the z and θ directions.

That the ram's horn was transversely isotropic about r , and not, for example, tetragonal, was confirmed by measurements on two wedges cut in the θz plane with their lengths at about 30° to z . These measurements were made later, under less favourable conditions, and were less accurate. However, they gave as the value of the dilatational velocity in the θz plane, at 60° to z , about 2.7 or 2.8×10^5 cm/sec, as for propagation parallel to θ or z .

Measurements were also made on a wedge cut with its length parallel to z and its faces at 45° to r and θ . Propagation in this case was poor; the velocity was in the neighbourhood of 2.5 or 2.6×10^5 cm/sec and was definitely less than 2.7×10^5 . Here the orientation was such that the method was not strictly applicable, and the result is only of qualitative value.

The transverse isotropy of ram's horn about r was further confirmed by independent measurements of the velocity of propagation of a dilatational pulse along each of the crystallographic axes of specimens cut in the form of small slabs a few millimetres thick. The frequency was 4 Mc/s. The author was enabled to make these measurements by the kindness of Dr. G. Bradfield, of the National Physical Laboratory (U.K.), who permitted the use of his apparatus, a modified form of that described previously (Bradfield 1950). The absolute values so determined are not directly comparable with those of Figure 1 and Table 1, since in the N.P.L. method it is necessary to apply considerable static pressure to the specimens, whereas none is applied in the total reflection method. However, it is clear that within the accuracy of the measurements $c_{\theta\theta} = c_{zz} > c_{rr}$, as found by the total reflection method.

V. CORRELATION OF ELASTIC ANISOTROPY WITH STRUCTURE

The most complete of the elastic data obtained are those for ram's horn and rhinoceros horn. The histological structure of each is shown diagrammatically in Figure 2. The cortex of ram's horn is composed of flat cells lying with their faces perpendicular to r . When a thin section cut in any direction was treated with concentrated sulphuric acid the cells separated immediately into layers perpendicular to r , but their separation into individual cells was much slower. It is therefore clear that histologically the structure is approximately transversely isotropic about r .

According to Rudall (1936), when keratin occurs in the form of flat cells the fibrils run in the plane of the cell either in a dispersed manner about z or else predominantly in two directions inclined at equal and opposite angles to z . Rudall has found that in cow's horn this angle is about 30° . For cow's horn the X-ray diffraction data (Astbury and Sisson 1935; Rudall 1936) show an α -keratin structure poorly oriented along z , with complete transverse isotropy about z . Rudall considers this compatible with the generally accepted view

TABLE 1

DILATATIONAL ELASTIC CONSTANTS c_{ii} AND DILATATIONAL WAVE VELOCITIES ω_d FOR SOME FORMS OF α -KERATIN

Material	Direction of Propagation	Specimen	$\omega_d \times 10^{-5}$ (cm sec ⁻¹)			$c_{ii} \times 10^{-11}$ (dyn cm ⁻²)
			Mean	Likely* Range	Extreme* Range	
Ram's horn	r	IV	2.53	2.58-2.47	2.61-2.41	0.844
			2.58	2.63-2.53	2.68-2.47	0.880
			2.63	2.67-2.60	2.73-2.49	0.879
		VI	2.58	2.61-2.55	2.70-2.48	0.850
			2.51	2.53-2.51	2.53-2.51	0.802
			2.53	2.56-2.49	2.56-2.49	0.812
		XI	2.80	2.83-2.78	2.88-2.75	1.029
			2.77	2.83-2.70	2.87-2.68	1.004
			2.80	2.81-2.79	2.81-2.79	1.029
	θ	I	2.79	2.84-2.76	2.87-2.72	1.022
			2.76	2.79-2.73	2.79-2.73	0.998
			2.76	2.85-2.71	2.85-2.71	0.990
		III	2.77	2.79-2.71	2.82-2.71	0.996
			2.71	2.74-2.67	2.74-2.67	0.964
			2.78	2.81-2.74	2.82-2.74	1.002
		V	2.81	2.88-2.78	2.88-2.78	1.027
			2.79	2.85-2.70	2.85-2.70	1.031
			2.71	2.68-2.73		0.959
	z	VII	4	Small		0.922
			1	2.85	2.82-2.88	1.057
			2	2.84	2.78-2.90	1.050
		VIII	5	2.89	Small	1.070
			6	2.86	Small	1.048
Ram's horn; pulse measurements	r	3	2.71	2.68-2.73		0.959
			4	Small		0.922
			1	2.85	2.82-2.88	1.057
	θ	2	2.84	2.78-2.90		1.050
			5	2.89	Small	1.070
			6	2.86	Small	1.048
	z	5	2.89	Small		1.070
			6	2.86	Small	1.048
Rhinoceros horn	l	I	2.47	2.51-2.44	2.53-2.42	0.797
			2.48	2.53-2.42	2.60-2.41	0.806
			2.60	2.66-2.56	2.67-2.55	0.875
		IIa	2.60	2.65-2.51	2.73-2.47	0.855
			2.56	2.62-2.51	2.67-2.48	0.846
			2.63	2.64-2.63	2.64-2.63	0.894
	s	IIb	2.63	2.64-2.61	2.71-2.58	0.894
			2.58	Small	2.61-2.55	0.861
			2.90	2.92-2.88	2.95-2.86	1.086
		IIc	2.92	3.03-2.84	3.03-2.84	1.101
			2.93	2.95-2.92	2.95-2.92	1.107
			2.92	2.93-2.91	2.93-2.91	1.101
		IIIa	2.87	2.89-2.83	2.89-2.83	1.059
			2.89	2.94-2.86	2.94-2.86	1.078
Baleen (whale-bone) from a rorqual	θ	II	2.49	2.51-2.47	2.52-2.46	0.802
			2.88	2.90-2.84	2.92-2.82	1.072
			2.85	2.87-2.83	2.89-2.80	1.046
			2.87	Small	2.92-2.83	1.065

TABLE 1 (Continued)

African porcupine quill cortex, boiled side wall	θ z	Several Several	≈ 2.6 ≈ 3.1	2.7-2.4 3.2-3.0	Unknown Unknown	≈ 0.9 ≈ 1.3
Same, tip, unboiled	θ z	Two specimens Two specimens	≈ 2.9 ≈ 3.4	3.0-2.7 3.5-3.3	Unknown Unknown	≈ 1.1 ≈ 1.5

*See text for definition.

†The ranges of c_{ii} are shown in Figure 1.

that the chains of the α -keratin structure lie along the fibrils, since the dispersion of the fibril directions is too great to permit the diffraction pattern to be resolved into two patterns crossed at 30°. The structure of ram's horn is very similar, except that the fibrils appear to be dispersed or crossed about z at angles up to about 20° from z . No orientation of the side-chain and backbone directions in the plane normal to z has been detected for any form of α -keratin. Molecularly, therefore, ram's horn is poorly oriented, but its average structure is one of transverse isotropy about z .

The data given here for ram's horn therefore show that the elastic anisotropy is predominantly determined by the histological rather than by the molecular structure. This illustrates the invalidity in general of direct argument from the elastic properties to the molecular structure in histologically complex materials.

Rhinoceros horn is also formed of flat cells, but they are arranged in concentric layers in component cylindrical structures which frequently are medullated (Fig. 2). These structures, which are tightly packed together, are of the order of 300-500 μ in diameter. The medullae, which are frequently flattened into a dumb-bell shape, do not show any marked preferential orientation with respect to the l and s axes. When thin sections were treated with concentrated sulphuric acid, there was instantaneous swelling and the cells peeled off in layers concentric with the cylinders. Over a macroscopic volume of rhinoceros horn, therefore, the histological structure is transversely isotropic about z . The molecular structure, as in horn, would be expected to be transversely isotropic about z , so that the histological and the molecular anisotropy are similar and should result, as is in fact observed, in an elastic anisotropy of the same kind.

The structure of baleen (whalebone) varies across the thickness (r) as shown in Figure 2 (Fraser 1952). The portion which was used for this study was the smooth outer layer, known as the "cut," in which the cells are flat and lie perpendicular to r . Wedges were prepared by removing the fibres from the inner side with a shaper. As the maximum thickness of the cut was about 1.5 mm, no wedges could be made with their width parallel to r , so that c_{rr} could not be measured. The wedges so prepared still showed a coarse striation of the same order of size as the fibres, and microscopic examination showed that on the (formerly) inner surface the cell layering was curved in the region which had been in contact with the fibres. On treatment with concentrated sulphuric acid the cells peeled off in flat layers perpendicular to r , but it was noticeable that there was a considerable difference between the θ and z directions. Swell-

ing was greater parallel to θ than to z , and the layers split more easily parallel to z than to θ . In some cells the fibrils ran predominantly along the z direction, in others they were crossed, and frequently they were invisible.

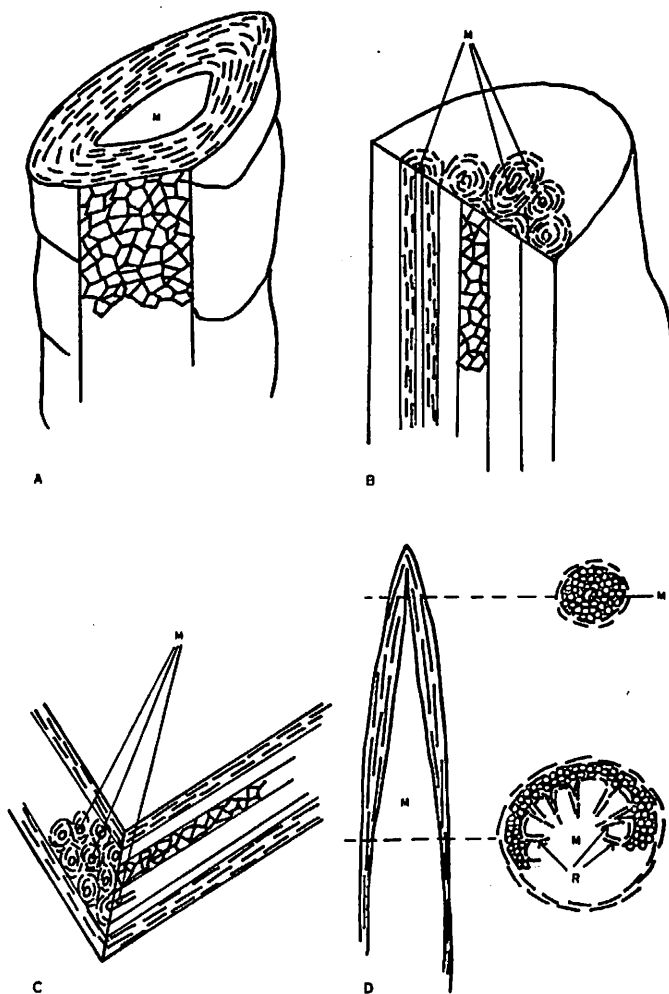


Fig. 2.—Histological structure of some forms of α -keratin: purely diagrammatic and not to scale. *a*, Ram's horn; *b*, rhinoceros horn; *c*, baleen (whalebone); *d*, African porcupine quill. *M* denotes the medullae and *R* the rays (see text).

This structure is correlated with the measured elastic constants, which show $c_{zz} > c_{\theta\theta}$. As explained above, c_{rr} could not be measured.

The cortex of African porcupine quill also has a complicated structure (Rudall 1936). At the tip it consists (see Fig. 2) of spindle-shaped cells lying parallel to z ; further down the quill it consists of three layers, a thin layer of

flat cells enclosing spindle-shaped cells, inside which there are again flat cells surrounding the medulla and forming the rays. Most of these inner flat cells were removed in the preparation of the specimens. On treatment with concentrated sulphuric acid the cells tended to break loose in blocks between the roots of the rays. As a secondary stage they peeled off into flat sheets with marked striation parallel to z and occasional striation perpendicular to this. These sheets were predominantly parallel to θz , but curved round towards the rz plane near the edges of the blocks. At a still later stage the sheets broke up parallel to z into spindle-shaped cells. The structure may be summarized as a sandwich of spindle-shaped cells between flat cells, all three layers being composed of sheets which lie predominantly parallel to θz , but with a tendency to form cylindrical blocks between the roots of the rays.

Histologically, therefore, the structure of the tip is transversely isotropic about z , and that of the opened-out side wall is orthorhombic. In spindle-shaped cells, according to Rudall, the fibrils, along which lie the molecular chains, run along the z axis and there is again no preferential orientation of the side-chain and backbone directions in the $r\theta$ plane, so that molecularly both the tip and, to a first approximation, the side wall should be transversely isotropic about z . This has been confirmed for the tip by the X-ray diffraction studies of MacArthur (1943). The few elastic data obtained (see Table 1) are of very low accuracy and show only that $c_{zz} > c_{\theta\theta}$ and that the degree of anisotropy is quite high. This conclusion applies also to the specimens boiled under pressure, although their structure may have been changed by the treatment.

VI. RELATION TO RESULTS OBTAINED BY OTHER WORKERS

The dilatational moduli c_H have not previously been measured for any form of α -keratin. Measurements have been made of some of the Young's moduli, which for isotropic solids with Poisson's ratio 0.25 would be about 17 per cent. less than the dilatational moduli measured under the same conditions.

The only measurements yet published on any of the materials used here are those by Warburton (1948), who measured the Young's modulus of sheep's horn in the θ direction (E_θ) as a function of regain, at low audio frequencies. He found that at 12 per cent. regain (which corresponds to a relative humidity in the neighbourhood of 50 per cent.) E_θ was approx. 0.5×10^{11} dyn cm $^{-2}$. This is much lower than the value, about 1.0×10^{11} dyn cm $^{-2}$, reported here for the dilatational modulus, as is to be expected, since all the available evidence shows that the moduli increase with frequency, at least in the range from 0 to 100 kc/s (Chaikin 1953). This increase is presumably due to the blocking of the slower relaxation processes.

Chaikin (1953) quoted Terry and Woods (unpublished data) as having measured the velocity corresponding to the Young's modulus in the z direction of "horn" at 50 kc/s. The value they obtained was $2.0_5-2.2_3 \times 10^5$ cm sec $^{-1}$, which corresponds to values of E_z from 0.55 to 0.65×10^{11} dyn cm $^{-2}$. The humidity was not specified. In a personal communication, Dr. Terry has given the mean velocity parallel to z in cow's horn at uncontrolled room humidity as

$2.15 \times 10^5 \text{ cm/sec}^{-1}$, which with $\rho = 1.3 \text{ g cm}^{-3}$ gives $E_z = 0.60 \times 10^{11} \text{ dyn cm}^{-2}$. These values lie between Warburton's low frequency value for E_θ and the high frequency (5 Mc/s) value obtained here for the dilatational modulus parallel to either θ or z .

There have been numerous determinations of the longitudinal Young's moduli E_z of keratin fibres; these have been surveyed by Chaikin (1953). The highest frequency used was that which he used himself, 102.5 kc/s. At 65 per cent. relative humidity and 22.2°C he found that for human hair the longitudinal Young's modulus E_z was about $0.84 \times 10^{11} \text{ dyn cm}^{-2}$, increasing slightly as the humidity decreased. The value for Lincoln wool was of the same order. If the Poisson's ratios of the forms of keratin considered are close to 0.25, this value of E_z is close to those which could be deduced from the dilatational constants c_{zz} of ram's and rhinoceros horn at 5 Mc/s by treating the materials as approximately isotropic. It is possible, therefore, that dispersion is small (relaxation processes becoming less important) between 100 kc/s and 5 Mc/s, but this cannot be regarded as established until further data are available.

VII. CONCLUSIONS

The most important conclusion to be drawn from this study is the qualitative one that the elastic anisotropy of keratinous solids in the region of small strains depends at least as much on their histological as on their molecular structure, even at so high a frequency as 5 Mc/s. It is found that ram's horn is transversely isotropic about the radial direction, and that rhinoceros horn is at least approximately transversely isotropic about the fibre direction, and this difference is correlated with the histological structure of the two materials. The approximate values of the elastic constants corresponding to the propagation of dilatational waves along the r , θ , and z directions respectively are: for ram's horn: 0.85, 1.01, and $1.01 \times 10^{11} \text{ dyn cm}^{-2}$; for rhinoceros horn: 0.80, 0.87, and $1.09 \times 10^{11} \text{ dyn cm}^{-2}$.

The anisotropy of baleen also appears to be correlated with its histological structure. The elastic constants determined for propagation parallel to θ and z respectively are approximately 0.80 and $1.06 \times 10^{11} \text{ dyn cm}^{-2}$.

Some very approximate data are also presented for the cortex of African porcupine quill.

VIII. ACKNOWLEDGMENTS

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