STRUCTURE AND SYNCHRONIZED STRETCH-ROTATION OF HAIRKERATIN FIBRES

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The theories concerning the stretching of hairkeratin fibres are briefly reviewed. The author's rotation method is described in detail and the explanation of load-rotation curves in terms of atomic structure is attempted.

NOT MANY albuminous bodies have been as successfully examined for their micro- and macro-structure as hair and wool keratin. Chemical, optical and mechanical methods of measurement were used in this task. The latter, especially, figured in many publications of the last 30 years, so that the special term "Mechanochemistry" was coined for the mechanical methods of measurement, and it is surprising that Mechanochemistry could have been so successfully used without anyone being completely clear as to its mechanism to this very day.

It therefore seems desirable to find a method which would sufficiently clarify the nature of the stretching process to allow the elimination of the most improbable theories hitherto adhered to. Knowledge of the real causes of stretching would lead to a truer picture of the structure of keratin, which in its turn could serve as a pattern for other proteins. All physicochemical experiments, especially Speakman's[1], have shown that the characteristic physical behaviour of keratinous bodies, such as their great elasticity, was dependent on their chemical structure. Three theories have to be examined, experimentally if possible.

The *Intercellular* Stretch Theory[1,2,3]

According to this theory it is not the spindle cells, the actual bearers of keratin themselves, but the amorphous connecting substance which lies between them that is responsible for the elasticity of animal and human hair. This theory can be mathematically deduced from load-stretch curves (*Fig. 1*)[4], and it postulates that during the initial stretch the "gliding surfaces" of two neighbouring cells are held together by a "putty substance" which breaks at the first kink in the curve and becomes merely a lubricating substance. The sliding of two neighbouring cells during further stretching corresponds to the end part of the stretch curve. The middle part of the curve would correspond to the jump from the elastic stretching of the putty

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substance to the continuous and more or less uniform sliding of the cell walls.

Other authors have tried to explain the three parts of the load-stretch curve by assuming that they express the mechanical properties of three distinct phases of keratin, K_1, K_2 and K_3, which lie partly or completely outside the cells and which differ from each other by their side chain.[5]

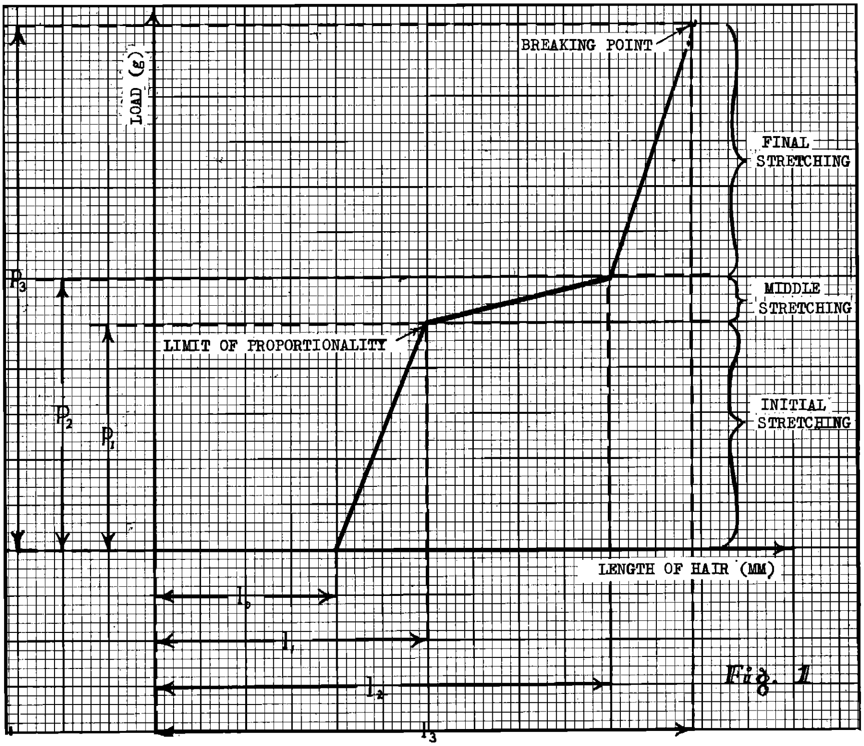


Fig. 1

The *Intermolecular* Stretch Theory

This theory explains the elastic behaviour of keratin fibres by an intermolecular overlapping. The substance between the molecules need not contain anything foreign but could be a constituent of keratin itself, such as polypeptide chains which are coiled along the axis of the molecule and which impinge on the neighbouring molecules by means of cystine side-arms or other side chains. Thus an endless, possibly two-phase, macromolecule is built up from smaller elements. The stretching would then consist of the dissolution of connecting bonds, would be dependent on the displacement of polypeptide chain networks[6] and would be characterized by the deformation of the crosslinks. There is an overlapping of the first-named theory and this one, since it is difficult to decide where the border between intermolecular and intramolecular displacement lies, without knowing the exact structure of keratin. If, for instance, in the complex polypeptide cables the single strands of the cable are connected by bridges, the uncoiling of the cables would be intramolecular, but if they are not connected, intermolecular.

The *Intramolecular* Stretch Theory

This theory attributes the elasticity to the uncoiling of more or less coiled or folded polypeptide chains or spirals[7] or even "superspirals", i.e., spirals the longitudinal axis of which is itself coiled in a spiral.

METHODS

In the following experiments, the rotation method, which was described elsewhere[8] has been utilized. This depends on the observation that the human hair rotates around its own axis when stretched, by suspending it from one end and attaching a weight to the other. The measuring device used was a load-stretch balance, as illustrated diagrammatically in *Fig.2*[9,10].

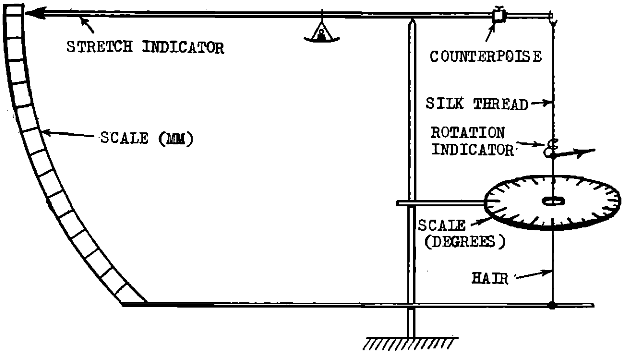


Fig. 2

The following is important to ensure the success of the experiments :

The hair which is to be measured should not be attached directly to the balance, but should be connected by means of a wire hook to a 100 mm long silk thread, the other end of which is tied to the arms of the balance. (Length of hair $l_0 = 50$ mm.) A pointer on the wire hook moves across a circular scale, through the centre hole of which the hair is passed to a clamp at the bottom. The loading must be carried out in the following manner :

A 5 g weight is put on the balance pan while the pointer is arrested on the nearside arm. When released, the weight causes stretching which can be read off on the "length" scale, and a rotation which can be read off the circular scale. A further 5 g weight may be added to the pan only after the stretching and rotating has ceased, which takes at least 20 seconds.

If the rotation of the hair "n" (degrees of rotation from zero, multiplied by π and divided by 180) is plotted against the load, a three-part load-rotation curve, more or less identical with *Fig. 1,* is obtained in which "n" is substituted on the abscissa for the length readings. In *Fig. 3* the two are drawn next to each other in order to illustrate the similarity of the two functions, load-stretch and load-rotation. It must be pointed out at this stage that the virtual identity of the two has been confirmed mathematically.

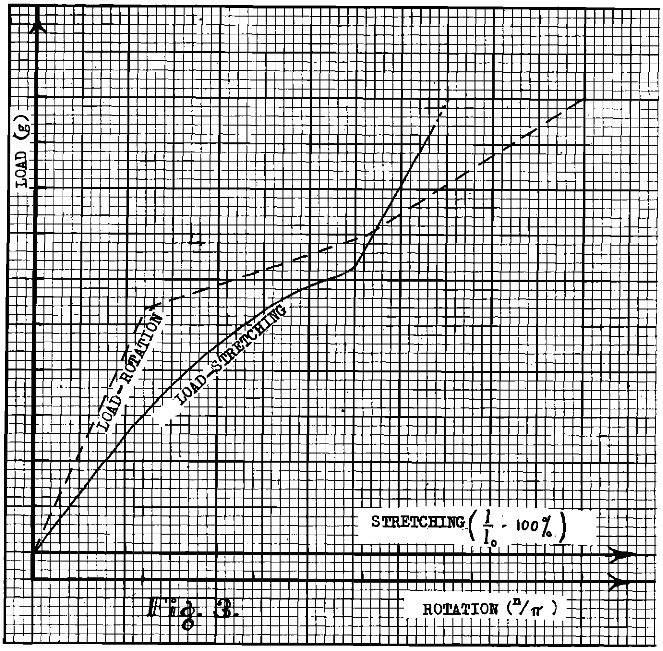


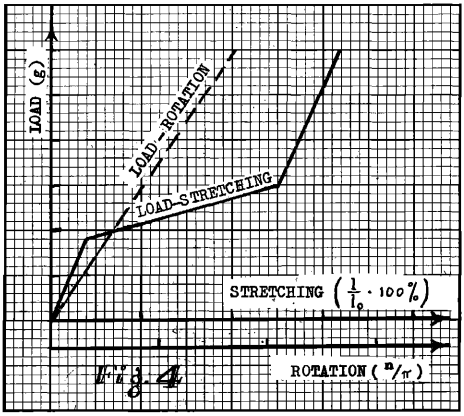
Fig. 3.

RESULTS

It may be generally inferred from numerous measurements of various types of hair that lengthening, i.e., stretching, is closely connected with a rotation around the longitudinal axis, i.e., that the hair becomes uncoiled. Such a joint lengthways-rotational movement can only be carried out by spiral or helical elements, no matter where these elements are situated. According to Heilingötter[11,12] the rotation corresponds to a left-handed screw. Without taking into consideration any of the observations mentioned below, results do point away from any inter-fibrillar theory, since with straight hair the fibrils on the whole lie parallel to each other and also to the longitudinal axis. It seems even less justified to blame the bilateral structure[13] of keratin for the rotational phenomena, since in that case the rotation of hair would be more likely to be a function of the Paracortex–

Orthocortex turning, which causes curling of hair, than a function of stretching. In reality the rotation was observed even in completely uncurled, sleek hair. It was always a function of the stretching, which has presumably very little connection with natural hair torsion. If the cellular structure of hair may be assumed as being orientated in a semi-parallel manner and if the desired spiral element is not to be found in histological structure visible under the microscope, then the unwinding of these spirals must cause a coiling of the superimposed parallel cords structure. In fact, one can see with the naked eye that hair will curl in a corkscrew manner if it is allowed sufficient freedom of movement during stretching. This is the case in the experiment described above, where the silk thread offered almost no resistance to the rotation of the hair. The small rotation of the silk thread due to the twist of its strands can easily be determined in the same way and deducted from, or added to, the result. Many results obtained from load-stretch measurements can also be used as approximate measurements of rotation. Are there any cases in which there is a discrepancy between the two processes? One immediately thinks that the α-β-keratin transition is not primarily connected with the triple stage load-stretch curve, as has been proved by X-ray examinations of horse hair. For this reason it would be useful to treat hair with reagents which have a specific action upon it and then to subject the hair to load-stretch rotation measurements. It has already been stated elsewhere[14] that in order to make the two measurements differ from each other, even after the hair has been dried, it is necessary to treat the hair for a quarter of an hour with ammoniacal thioglycollate solution.

The separation of cystine- and salt-bonds appears on the load-stretch graph as an increase of the middle section, but the load-rotation curve does not follow this pattern. In that graph, the rotation throughout the entire process is constant at about $2\pi/5$ g weight increase and there is no increase in the rotation anywhere to indicate a middle section. An equivalent treatment with ammonia, without an added reducing agent, causes no substantial change in the curves and therefore one is justified in concluding that the breaking-up of the cystine bridges removes the synchronization of longitudinal and rotational movements. The unwinding of the spiral units must therefore be related to cystine, at least in the non-elastic region of stretching. If this supposition is correct, then other reactions must also influence the relation of stretch to rotation, if cystine is involved in any way. To test this, the influence of hot sodium bisulphite was examined. Unfortunately, the fully contracted hair was weakened to such an extent that it was unsuitable for further experiments. For this reason, the time of treatment with 5 per cent sodium bisulphite solution was reduced to 10 minutes at a temperature just below boiling point. This caused a reduction of stretchability from 54 per cent to 13 per cent (measured after drying). Only one strand of hair withstood the treatment sufficiently well to yield a three-part stretch curve, after drying and conditioning to constant humidity. Even in this single instance the rotation curve remained a straight line and did not possess the middle section of the corresponding stretch curve (*Fig. 4*).



In this case, as with hair reduced by mercaptan, the synchronization of the stretch and rotational movement is partially destroyed, and this proves that with treated hair the load-stretch behaviour can be normal, while the load-rotation graph loses its three-step consideration.

Reduction of boiling time to 5 minutes made no difference, but a reduction of temperature from 97° C to 67° C was sufficient to give the normal load-stretch and load-curves. These graphs thus resemble those obtained after 10 minutes' boiling in distilled water, except that the middle section of the curve of the bisulphite-treated hair was longer. In the load-stretch curve the middle section increased from 18 per cent to 22 per cent, and in the load-rotation curve from 720° to 780°. The following quantitative results may be of interest : During the initial stretching of hair EH34, the free end of 50 mm long untreated hair rotated an average of 568°/mm or 72·5°/g. Altogether the rotation to the extrapolated tear point is 6,410° at 87·5 g, i.e., 72°/g, or $17\frac{1}{2}$ complete turns with a lengthening of 60 per cent. It was necessary to add 5·5°/g to the result, in order to compensate for the rotation of the silk thread which turned in the opposite direction. Hair treated with a reducing agent also turned through approximately 70°/g up to its tear point, but did not reach the same total of rotation since it tore much sooner.

The identity of stretch and rotation or behaviour becomes obvious when the stretch values arrived at by the "Bonitation" method[15] are mathematically compared with those obtained by the rotational method. According to the "Bonitation" method the "stretch-factor" (hair index) *Hi* is defined as the sum of deviations of the fibre flaws, in the three regions of the curve, from those of a standard hair, and when using symbols designed in *Fig. 1* and *Fig 3* the following formulation is arrived at (derived from[9,15]):

$$Hi = \frac{l_1 \,.\, 100}{l_0 \,.\, P_1} + \frac{l_2 \,.\, 122}{l_0 \,.\, P_2} + \frac{l_3 \,.\, 184}{l_0 \,.\, P_3} - 6 \; (g^{-1}) \qquad (1)$$

Hi is then multiplied by the average cross section of the hair (mm^2). The corresponding "rotational factor" *Hir* is defined as follows

$$Hir = \frac{n_1 \,.\, 100}{l_0 \,.\, P_1} + \frac{n_2 \,.\, 122}{l_0 \,.\, P_2} + \frac{n_3 \,.\, 184}{l_0 \,.\, P_3} - 6 \qquad (2)$$

$$\text{where } n_{1,2,3} = \frac{a_{1,2,3} \,.\, \pi}{180} \qquad (3)$$

In an ideal case, *Hi* equals *Hir*. The degree of synchronization can be mathematically calculated by defining deviations as $QHir = \frac{Hir}{Hi}$.

If hair of different origin is compared quantitatively in this manner, many difficulties are encountered. Both the *Hi* values and the synchronization of rotation and stretch are affected by the origin of the hair, and the state of health of the person to which it belongs[16] [17] [18] and they deviate more or less from standard values, i.e., *QHir* deviates from unity. For example, hair EH34 (woman on the fifth day of her period) and EF18 (young man with chronic nephritis) as cited in *Table 1.* The degree of synchronization *QHir* deviates in each case from the ideal value in an entirely different manner. The average rotation/mm stretch over the whole curve is 304·5° in the former case and 87·4° in the latter.

Having accepted an explanation of the changes in stretch values in terms of chemical processes, one has to decide whether to place the stretch-rotation processes into cystine-containing extracellular regions or into regions which cannot be observed by X-ray, or whether the values of Crick's[19] "Super Screw" or Pauling's and Corey's[20] "Complex Screw (compound helix)", obtained through X-ray examinations, are not treated as fixed natural constants but as statistical averages, which allow upward or downward deviations. These could vary to the extent of ± 2° when determining valency angles[21] and the macroscopical effect would be greatly magnified.

To continue with these thoughts, one could try to explain that the three parts of the load-stretch curve are due to a complex process. The α-β-isomerization could be attributed to unfolding of structural elements.

The rotation of the hair, which is roughly $2\pi/5$ g in the highly elastic Hooke's region, remains even when the middle and end parts of the curve disappear, owing to the breaking of crosslinks. In that case, the whole of the load-rotation curve becomes a Hooke's curve (*Fig. 3*). From this, one must conclude that the process is continuous from the beginning to the breaking point, and is not replaced at the limit of proportionality by a different process but is superimposed upon it. The first part of the process is not therefore connected, or only slightly so, with cystine length. It could easily be due to the primary polypeptide spiral. The second part of the process superimposed upon it always occurs as part of the load-stretch curve. It only occurs in the load-rotation curve if the hair is untreated. It would appear as if the component loses its spiral character when the crosslinks are removed, or as if an element could be simply pulled out, instead of having to be screwed out with a rotational movement, after the links have been broken. Many a mystery could be explained if during this process the β-screws of the *AB6* strands[20] which turn in the opposite direction to the central, automatically twisting *A* screws, took part in this. The element which starts moving from the limit of proportionality seems to be connected by cystine bridges with the element which is untwisted from the beginning of the process. The results obtained with human hair cannot be assumed to automatically extend to animal hair. Experiments with the latter, like studies with other high polymers appear promising, judging by the work of Goldworthy and Lang[22]. These authors measured the velocity of the rotation of wool fibres in both directions, weighted with 6 mg in various fluids, and explained the rotation in terms of the relaxation of pre-existing tensions.

EXPERIMENTAL DATA

To explain symbols not yet elucidated in *Figs. 1–3* and Formulæ 1–3 :

$$A = \%\ \text{length of the initial stretch} = \frac{l_1 - l_0}{l_0} \cdot 100\ (\%) \qquad (4)$$

$$M = \%\ \text{length of the middle stretch} = \frac{l_2 - l_1}{l_0} \cdot 100\ (\%) \qquad (5)$$

$$T = \%\ \text{length of breaking stretch (not final stretch)} = \frac{l_3 - l_0}{l_0} \cdot 100\ (\%) \qquad (6)$$

Ar, *Mr* and *Tr* are the rotational values in degrees, taken from :

the initial stretch $= n_1$
the middle stretch $= n_2 - n_1$
the breaking stretch $= n_3$

Pr are the *P* values of rotation.

As each experiment consisted of several measurements, only the average of each experiment is quoted. All experiments at constant humidity.

Experiment 1 Blank with untreated hair EH34.
2 Hair EH34 after boiling in water for 10 minutes.
3 Hair EH34 after treatment with 5 per cent sodium bisulphite at 67° C for 5 minutes.
4 Hair EH34 after treatment with 5 per cent sodium bisulphite at 97° C for 5 minutes.
5 Hair EH34 which was thrown into 5 per cent sodium bisulphite solution at 65° C. The latter was brought to the boil by steadily raising the temperature for 10 minutes.
  a. Coarse hair, and
  b. Thinner hair.
6 Blank with untreated hair EF18.
7 Hair EF18 after ¼ hour's treatment with conc. ammonia.
8 Hair EF18 after ¼ hour's treatment with ammoniacal thioglycollate, rinsing subsequently. The strength of the solution was 10·06 per cent in respect of thioglycollic acid—*p*H : 9·5 (Merck special indicator).

TABLE 1

Expt. No.	*Hi*	*Hir*	*QHir*	A	M	T	Ar	Mr	Tr	P_1	P_2	P_3	Pr_1	Pr_2	Pr_3
1	1·7	4·9	2·9	12·3	20·5	54	59·5	30	110·5	50	62·5	87·5	47·5	60	87·5
2	3·4	3·5	1·0	12	18	58	52	12	82	45	55	75	45	50	75
3	1·8	3·2	1·8	11	22	61	57	13	99	50	60	95	50	55	95
4	∞	∞	1	—	—	12	—	—	52	—	—	40	—	—	40
5a*	8·4	∞	∞	4	20	32	—	—	49	20	30	60	—	—	60
5b	∞	∞	1	(9)†	—	13	—	—	50	(30)†	—	35	—	—	35
6	10·9	7·4	0·68	8	17	60	22	9·4	46	20	25	55	20	25	55
7	11·1	7·0	0·63	20	21	72	23	9·5	52	20	25	55	20	25	55
8	34·8	∞	∞	10	90	190	—	—	31	15	20	25	—	—	25

* Only 1 determination of all values.
† Only 1 determination of this value.

To show the number of measurements which were taken to arrive at the above results, the data of a single experiment are given in Table 2, and the results derived therefrom in Table 3.

TABLE 3

Hi	*Hir*	*QHir*	A	M	T	Ar	Mr	Tr	P_1	P_2	P_3	Pr_1	Pr_2	Pr_3
3·5	14·9	4·3	6	20	44	151	140	401	35	51	75	35	50	75

TABLE 2

Load g	Degrees of rotation	Correction for silk thread (0·1 g)	Degrees of net rotation	% Rotation per length unit $\frac{n \cdot 100}{l_0}$	% Increase in length per unit $\frac{l \cdot 100}{l_0}$
0	0	0	0	0	100
5	350	35	315	11	102
10	1130	265	865	30	103
15	1760	285	1475	52	104
20	2190	295	1895	66	105
25	2820	305	2515	88	106
30	3610	315	3295	115	108
35	4630	325	4305	141	109
40	6070	335	5735	201	113
45	7510	345	7165	251	117·5
50	8590	355	8235	291	126
55	9660	365	9295	325	134·5
60	10380	375	10005	350	140
65	11080	385	10695	374	144·5
70	11530	395	11135	389	148
75 (exp.)	(11860)	(405)	(11455)	(401)	(151)

SUMMARY

Elongation of human hair, due to a steadily increasing load, occurs together with a rotational movement. This leads to a twisting of hair if one end is fixed and the other one allowed to move freely. The degree of synchronization between the longitudinal and rotational movements during the folding over of the elements of keratin can be expressed mathematically by a quotient of the rotational stretch factors. This depends on the condition of the cystine bridges.

The stretching movement and the rotational movement take place in different elements of keratin, of which at least two must possess a spiral structure. The highly elastic initial stretch can occur in the line of rotation of a polypeptide spiral, independently of the cystine lengths. Starting from the limit of proportionality it is probable that a folding of the superimposed structures takes place, the rotational-stretch movements of which are synchronized by cystine bridges. When the cystine bridges are destroyed by chemical action, the load-rotation curve follows Hooke's law to the breaking point. If *AB6*-strands affect both cases, then cystine bridges may well link *A* and *B* screws. It is possible that the structure of the complex helixes is not fixed but variable around a statistical average.

DISCUSSION BY G. T. WALKER

The data presented above are of very considerable interest and importance to those who are engaged in research on hair. The load-rotation curves for various hair fibres are most illuminating, and these curves appear to be dependent upon the history of the hair and upon the actual health of the person from whom the hair is taken. It may well be that in the future we shall be able to obtain much valuable diagnostic information concerning a patient's state of health by appropriate load-rotation studies on the hair.

Hirsch has shown that, to some extent, the load-rotation curve is dependent upon the cystine disulphide bonding system which has long been known to be present in keratins. Reduction of the –S–S– bonds in hair with a reducing agent as thioglycollic acid, for instance, results in a complete change in the character of the load-rotation curve. This correlation between the load-rotation data and the reduction of the cystine disulphide bonds is of the greatest interest, and requires further intensive studies.

Hirsch, while not committing himself to any really definite interpretation of his load-rotational work, seems to suggest that an explanation of his findings may lie in the spiral configuration of keratin, as postulated by Pauling, *et al.*[7], or in the modified "coiled coil" theory of Crick[19]. In this connection, however, it is pertinent to mention the Huggins[23] structure for α-keratin, a theory which is probably the nearest approach to the real structure yet proposed. The interpretation of Hirsch's data in terms of the Huggins structure would be very difficult.

An objection to the idea that these load-rotational curves can be explained in terms of an atomic structure is that Hirsch's experiments are essentially macro experiments. To attempt to explain macro experimental data in terms of micro structure is always rather dangerous, and many will be suspicious of any such attempt. Indeed, we find in a recent paper by Heilingötter[11] an example of this kind of thinking. Heilingötter, in an effort to explain Hirsch's data, draws a parallel between the screw-like structure of hair and an ordinary metal spring. He draws the conclusion that the rotation of a hair fibre corresponds to that of a left-hand screw, and he draws that conclusion solely on the basis of load-rotation studies on these metal springs.

Any deductions about fine structure of hair fibres from macro mechanico-chemical experiments must be suspect, if only because the fine structure does not usually make itself felt at macro levels.

We have still to explain the influence of the disulphide bonding system in load-rotational work, and no explanation can be offered here.

It is of interest to mention the role of hydrogen bonds in the structure of α-keratins. Since these hydrogen bonds are of an intramolecular nature in α-keratin, playing an important part in the helical configuration of Pauling, it would be of very great interest to investigate the action on hair of active hydrogen bond "breakers", such as concentrated urea and lithium bromide solutions, with reference to the load-rotation curves. Break-down of the hydrogen bonds may well prove as important as cleavage of disulphide bonds in investigating load-rotation curves of hair fibres.

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THE EFFECT OF DECAMETHYLENE-BIS-4-AMINOQUINALDINIUM (DEQUALINIUM) SALTS ON THE GROWTH OF *PITYROSPORUM OVALE*

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Dequalinium salts restrict the growth of *Pityrosporum ovale* and other micro-organisms contaminating skin and hair. Preparations of Dequalinium are highly effective in the treatment of seborrhoea and infective dandruff.

INTRODUCTION

DANDRUFF IS characterized by the presence of loosely adhering scales on the scalp ; the scales are flakes of the stratum corneum or horny layer of the

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