LETTERS TO THE EDITORS

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Optical Rotation of the α-Helix in Synthetic Polypeptides

In a communication from this laboratory[1], the belief has been put forward that the polypeptide chains in poly-L-alanine fibres form right-handed rather than left-handed helices; this view is based on the X-ray diffraction pattern. If it is correct, it is to be expected that the same sense of helix will be the stable form in other L-polypeptides. Now the contribution to the optical rotation of an α-polypeptide from the helix alone is considerable; according to Fitts and Kirkwood[2], a right-handed helix of polyglycine should have a specific rotation of about + 130°. In a later communication[3] they have concluded from the change in specific rotation on destruction of the α-helix (in poly-γ-benzyl-L-glutamate and in poly-L-glutamic acid) that in these polymers the helices are right-handed.

The stability and sense of the α-helix can be examined by measuring the optical rotation of a series of polypeptides in which the proportion of D- to L-residues is varied. The addition of a proportion of D-residues, randomly arranged along a chain of L-residues in the α-helix form, will not affect the helix if this has a strongly preferred sense. The optical rotation of a predominantly L-polypeptide should therefore at first move towards higher positive values as the proportion of D-residues is increased, but must ultimately become zero when D- and L- residues are present in equal amounts.

We have measured the optical rotation of a series of D : L-leucine polypeptides in benzene at a concentration of 0·2 per cent (w/v). Films cast from these solutions showed the carbonyl infra-red absorption band in the normal position for the α-form. Since many of these polymers form gels under these conditions (even at 60° C.), small amounts of *m*-cresol (minimum 1 per cent, v/v) were added, and the optical rotation in pure benzene was obtained by extrapolation to zero concentration of *m*-cresol. This procedure was justified by measurements made in pure benzene, when the solubility allowed this. The addition of *m*-cresol lowers the positive rotation of the mainly L-polypeptides. Even with *m*-cresol present, it was found necessary to make measurements at 60° C. to avoid gel formation. It is convenient to express the results in terms of the residue rotation [*R*]

$$[R] = \frac{R}{100}\,[\alpha]$$

where R is the residue weight and [α] the specific rotation defined in the usual way. The results are shown in Fig. 1.

The expected effect is strikingly apparent, and the increase in rotatory power continues to a lower excess of L over D values than might have been anticipated. The increase in rotatory power is not caused by increasing instability of the α-helix as the proportion of D-residues becomes greater (leading to the formation of a random coil), because conditions which favour a random coil lower the positive rotation[4]. The linear part of the graph is readily accounted for

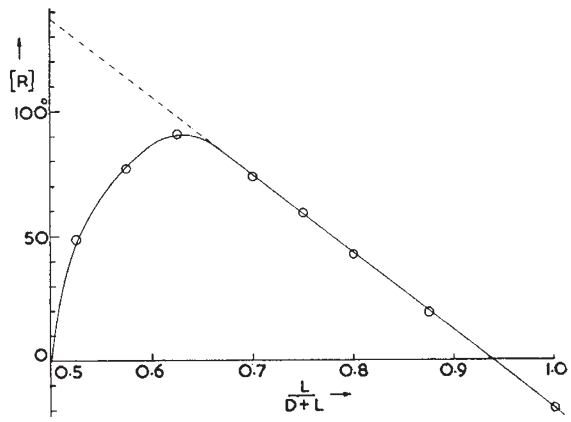

Fig. 1. Residue rotation of poly-leucine plotted against fraction of L-residues in polymer. Concentration 0·2 per cent w/v in benzene at 60° C.; $\lambda = 5893$ A.

if, over this range, all the polypeptide chains are right-handed, producing a positive rotation from the helix core, with the L- and D-side-chains giving respectively negative and positive contributions. The contribution from the helix core is given by the intercept on the *y*-axis, and corresponds to a residue rotation of + 138°. We may note that the corresponding value for poly-L-leucine in benzene calculated from Fitts and Kirkwood's formula is 70°.

Our experiments show clearly that, in solution, one sense of helix is significantly more stable than the other for a given enantiomorph. Together with Fitts and Kirkwood's calculation that the form optical rotation is positive for a right-handed helix, the results confirm that L-polypeptides form right-handed helices. The possibility that the optical rotation of an α-polypeptide can be treated as the sum of contributions from the helix core and the asymmetric centres is interesting, and may have applications in the case of proteins such as silks.

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Blood-Group Antigens on Human Epidermal Cells

Recently, Coombs, Bedford and Rouillard[1] reported that the A and B blood-group antigens are present on human epidermal cells. A series of skin samples has now been examined for blood-group antigens other than A and B by the method of mixed erythrocyte-epidermal cell agglutination described by these authors.

Suspensions of isolated epidermal cells were prepared by treating small fragments of stored, thin