

crease in the solubility of keratins in urea-bisulfite or thioglycollate solutions after such treatments. These changes in solubility have been attributed variously to disulfide rearrangement (Kessler and Zahn, 1958) and formation of lanthionine crosslinking (Lees and Elsworth, 1955). Whether or not such changes occur concomitantly, the exchange results support the suggestions of Speakman (1959) and Swan (1959) that the main cause of the decreased solubility lies in major conformational changes in the keratin.

A parallel for such conformational changes might be seen in the α - β transformation which occurs on heating poly-L-lysine at pH 10.8 (Applequist and Doty, 1962). A transformation of this kind occurs when keratin fibers are stretched and this change can be made permanent by steaming in the β state. In this state the urea-bisulfite solubility is reduced (Lees *et al.*, 1960). If β material were formed in keratin by heating in alkali, it would most probably be disorientated, and unlike the highly organized β structures of, say, feather keratin or silk fibroin, would be rapidly exchangeable.

Use of Exchange Data.—Two assumptions have frequently been made about hydrogen-exchange rates in keratins, namely, that *all* slow hydrogen atoms are located in the peptide bonds rather than the side chains, and that the ratio of slow hydrogens to fast ones can provide an estimate of the proportion of crystalline material in the keratin. Such assumptions are difficult to justify on the basis of exchange work on simpler systems (e.g., Harp and Eifert, 1960; Leach and Scheraga, 1958). The large number of slow hydrogen atoms and the nature of their temperature- and pH dependence make it unlikely that either assumption is applicable to keratins. The difficulties inherent in making estimates of crystallinity and the wide variations in these estimates have been reviewed by Fraser (1955), Fraser and MacRae (1958), and Peters (1963). Estimates vary from 10 to 60% depending on the method of measurement and the assumptions made in interpreting the estimates. In any event, the usefulness of these estimates is doubtful since the term "crystallinity" is open to several definitions. For example, insulin exchanges more readily with D₂O even in the insoluble, isoelectric, and highly crystalline state than does fibrous keratin which is considerably less "crystalline."

The present work suggests that 30 g-atoms of hydrogen (class II) are located both in side chains and in peptide bonds, 25 (class III) are probably in the peptide bonds of single helices, and 21 (class IV) are most likely the peptide-bond H atoms of multiple helices. An estimate of the proportion of polypeptide chains in the most stable, probably multiple-helical, form would be 21/105 or 20%. If the less stable hydrogen atoms of class III were included, the proportion of chains in both forms would be 46/105 or 44%. These estimates need bear no simple relationship to "crystallinity," but should be useful in comparative studies aimed at understanding the conformational changes

which accompany physical or chemical modifications of keratins. A point which arises from the pH dependence shown in Figure 4 is that comparisons of keratin-exchange data are best made in acid solutions where rates are slowest and differences are likely to be greatest.

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CORRECTION

In the paper by M. Rosell-Perez and J. Lerner, in Volume 3, No. 1, January, 1964, on p. 86, column 2, lines 22-23 "... converted to an I form (Fig. 7), ..." *should read*, "... converted to an I form (Fig. 4), ..." On pp. 87 and 88 the legends for Figs. 6 and 7 have been transposed; i.e., Fig. 6 appears on p. 87 with the legend to Fig. 7, and Fig. 7 appears on p. 88 with the legend to Fig. 6.

Through an error, the last article in the April, 1964 issue was omitted from the Table of Contents and the author's names were not included in the Author Index. The article, "Synthesis of *N*-Monomethyl- and *N,N*-Dimethylcephalins," by David Shapiro and Yechiel Rabinsohn, appears on page 603 of Volume 3, No. 4.