

of barium N-acetylglucosamine-6-sulphate. Barium N-acetylglucosamine-monosulphate, prepared by the direct sulphation of N-acetylglucosamine, was identical with barium N-acetylglucosamine-6-sulphate prepared by definite synthesis.

Further evidence as to the location of the sulphate group in position 6 of the hexosamine molecule was obtained by examining the behaviour of the compounds in the Elson-Morgan reaction¹³. Both authentic N-acetylglucosamine-6-sulphate and N-acetylglucosamine monosulphate gave 100 per cent colour production in this test using N-acetylglucosamine as standard. It has been shown that N-acetylhexosamines substituted in position 6 behave normally in the Elson-Morgan reaction whereas substitution in position 3 results in enhanced colour production. On the other hand, substitution in position 4 causes suppression of colour formation¹⁴. N-acetyl galactosamine monosulphate, prepared by direct sulphation of N-acetyl galactosamine¹¹, also gives 100 per cent colour formation in the Elson-Morgan test¹³, providing preliminary evidence of the location of the sulphate group in position 6 of the molecule.

A more complete account of this work, together with the results of enzyme studies, will be given elsewhere.

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Optical Rotation and Configuration of Poly-L-tyrosine

IN a recent communication from this laboratory¹ it was reported that the constant b_0 in Moffitt's equation² for the optical rotation of a helical polypeptide is positive for solutions of poly-L-tyrosine in dimethyl formamide and in pyridine, and for the sodium salt of this polymer in solution and in films. It was implied that in spite of the unusual sign of b_0 the polymer was in the α -helical form, and that the positive value is a consequence of the strong chromophoric group near the β carbon atom. We have since made further measurements of the optical rotation of a solution of this polymer in *N* sodium hydroxide and of films cast from a solution in dimethyl formamide at 60° C., together with observations of the infra-red

spectrum and X-ray diffraction pattern of the films. These studies have led us to the conclusion that it is more probable that in dilute solutions in pyridine, in dimethyl formamide, and in aqueous alkali, poly-L-tyrosine is in the random coil configuration, as is its sodium salt in films.

The optical rotatory dispersion results are difficult to interpret unambiguously, because of the unknown effect of the chromophoric groups in the side-chain. There is no reason for supposing that the λ_0 of the Moffitt equation will be the same as in other polypeptides, that b_0 will be zero for a random coil arrangement, or indeed that the Moffitt equation will hold at all. However, if one nevertheless takes the usual value of 2120 Å. for λ_0 and makes a Moffitt plot, one obtains values of b_0 of about +300° for a solution in pyridine, about +400° for solutions in dimethyl formamide and in *N* sodium hydroxide, about +550° for films of the sodium salt, and about -4000° for films of poly-L-tyrosine cast from dimethyl formamide. It is tempting to suppose that the configuration is different in the last case from that in the others, although the criterion is somewhat arbitrary. The distinction between the films cast from dimethyl formamide and the other systems gradually becomes less clear-cut as λ_0 is increased; however, so far as can be seen from measurements over a rather limited range of wave-length, the Moffitt plot gives the straightest line for a λ_0 of rather less than 2120 Å.

Since at pH 14 the polymer is completely ionized, it would seem unlikely that the solution in aqueous alkali contains a large proportion of the α -helical configuration. On the other hand, infra-red spectroscopy and X-ray diffraction provide some evidence that the films cast from dimethyl formamide contain polypeptide in the α -helix form. Such films, when rolled, have been found to show marked infra-red dichroism of the kind associated with the α -helix. However, this behaviour is not reproducible, some similarly treated films failing to show any dichroism. The X-ray diffraction pattern of α -helices of poly-L-tyrosine packed hexagonally would be expected to have a strong ring corresponding to an interplanar spacing of 11.1 Å., as may be calculated from the density of the films (1.254 gm./c.c.). The X-ray diffraction pattern of these films does indeed have a ring at 11.1 Å.; but it is not particularly strong. Heating the films *in vacuo* at 130-140° C. for 2 hr. apparently crystallizes the polymer, and the subsequent X-ray pattern does show a strong 11.1 Å. reflexion.

The results of these experiments are far from conclusive; but we feel that they strongly suggest that poly-L-tyrosine in each of the three solvents we have used, and its sodium salt in films, are in the random coil configuration, whereas in films cast from dimethyl formamide the polypeptide exists as α -helices.

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