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The crystal structure of silk fibroin.*

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In a recent issue of this journal Warwicker (1954) proposed a structure for silk fibroin which is not in agreement with the results of an investigation of the structure of silk fibroin which we have carried out and submitted for publication (Marsh, Corey & Pauling, 1954).

The structure proposed by Warwicker resembles the structure which we had derived in that it is based on antiparallel-chain pleated sheets packed together at spacings alternately 3·7 and 5·6 Å (our values being 3·5 and 5·7 Å); also, alternate residues in the polypeptide chains are glycine. The main features of our structure were described in a report to the Solvay Congress on proteins in April 1953 (Pauling, 1953). However, Warwicker's structure differs fundamentally from ours in that it is based on the orthorhombic space group $P22_12_1$ rather than the monoclinic space group $P2_1$ which we assigned to our pseudo structure with the same unit cell. At an early stage of our investigation we had considered this orthorhombic structure and had been forced to reject it because of its failure to give even approximate agreement between the observed and calculated intensities of principal equatorial reflections. Since Table 4 of Warwicker's paper purports to show that this agreement is satisfactory, it is necessary to point out the discrepancies that exist.

The outstanding discrepancies concern the intensities of the reflections 020 and 120 (Warwicker's indices). The strongest reflection on the X-ray pattern of silk fibroin is the medium-sharp equatorial reflection A_3 with spacing 4·3 Å. From photographs of doubly-oriented specimens prepared by Kratky & Kuriyama (1931) and by us (Marsh *et al.*, 1954) this reflection has been definitely shown to arise from sets of planes making an angle of approximately 70° with the plane of rolling of the specimen (identified with the plane of the pleated sheets). This angle and the observed spacing of 4·3 Å allow this reflection to be unambiguously indexed as 120. However, the intensity of 120 calculated from the parameters listed in Table 3 of Warwicker's paper is practically zero. On the other hand, the intensity of the 020 reflection, as calculated from Warwicker's parameters, is very large, whereas photographs of doubly-oriented specimens show that the observed intensity of 020 is, at most, only a small fraction of the intensity of 120 (see, for example, Kratky & Kuriyama, 1931, Figs. 2 and 4). These fundamental discrepancies are obscured throughout Warwicker's paper by his failure to treat reflections 020 and 120 individually.

Table 1. *Data for equatorial reflections of silk fibroin*

Reflection	$(\sin\theta)_o$*	$(\sin\theta)_c$	*hkl*	I_c	I_o
A_1	0·079±0·003	0·083	100	187	90
		0·116	110	1	—
		0·163	020	455	—
A_2	0·164±0·007	0·166	200	700	450
A_3	0·181±0·006	0·183	120	3	900
		0·185	210	4	—
		0·233	220	50	—
A_4	0·253±0·002	0·249	300	322	180
		0·259	130	2	—
		0·262	310	19	—
		0·296	230	2	—
		0·298	320	39	—
A_5	0·328±0·001	0·327	040	40	20
		0·332	400	28	—
		0·337	140	0	—
		0·342	410	3	—

* The uncertainties are estimated limits of error.

Intensities and values of $\sin\theta$ for the low-order equatorial reflections are listed in Table 1. Observed values of $\sin\theta$ and observed intensities were obtained from spectrometric measurements made on silk fibroin with Cu $K\alpha$ radiation (Marsh *et al.*, 1954); they are in close agreement with the observations of Kratky & Kuriyama (1931). The indices (based on Warwicker's unit cell) were assigned in accordance with the demands of photographs of doubly-oriented specimens. The intensities were calculated in the manner described by Warwicker from the parameters listed in his Table 3. Discrepancies between these calculated intensities and those listed by Warwicker in his Table 4 are apparently due to his having erroneously included the carbon atom C_1 twice in his calculations—once as C_1 and once as the identical atom C_6 (see his Table 3).

In view of the serious discrepancies between calculated and observed intensities of low-order equatorial reflections, the structure proposed by Warwicker for silk fibroin must be considered to be incorrect.

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