

the helical configuration of polypeptide molecules in solution⁸⁻¹⁰, and we have found it possible to use this technique for examining solid films. Films of poly-L-alanine show the anomalous dispersion of the α -helix. It is interesting that Moffitt's b_0 term (which indicates the presence of anomalous dispersion of optical rotation) has the same negative sign and about the same magnitude for poly-L-alanine films as for other L-polypeptides in solution, although the specific rotation in sodium light has a large negative value in the film and a positive value in solution. This shows the great effect of environment on the magnitude and sign of the rotation, and the comparative invariance of b_0 , as predicted by Moffitt. Poly-L-tyrosine, however, has a positive b_0 in solution in dimethylformamide and in pyridine; its sodium salt has also a positive b_0 (in film and in aqueous solution). We believe that the unusual sign of b_0 is a consequence of the presence of a strong chromophoric group near the β -carbon, so placed that it must to a great extent share the helical form of the core.

In films of water-soluble *Bombyx mori* silk fibroin, lysozyme and the sodium salt of poly-L-glutamic acid, the value of b_0 is so low as to be negligible, and this is taken as evidence of the absence, or at least low concentration, of the helical form. These films are not in the extended β -configuration however (as shown by the absence of a carbonyl band at 1,630 cm^{-1}). The silk films, even after intensive drying, show no peak in the spectrum at 3,460 cm^{-1} (the 'free' NH stretching mode), and it must be concluded that substantially all the peptide hydrogen bands are formed, in what appears to be a disordered state.

It is clear from these observations that a carbonyl band at about 1,660 cm^{-1} is observed in polypeptide spectra not only with the α -helix and collagen folds^{6,11} but also in what, in the absence of further evidence, seems to be a disordered state. In the case of some globular proteins, a certain amount of order presumably persists in solid films, but in lysozyme it is not of a kind which gives rise to anomalous dispersion of optical rotation. These results contrast with those found by Cohen and Szent-Gyorgyi¹² in muscle proteins, where in aqueous solution the α -helix configuration appears to be dominant.

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Mucopolysaccharides from Cartilage and Nucleus Pulposus

Meyer and Rapport¹ described the isolation from hyaline cartilage of two chondroitin sulphates, *A* and *C*. The only differences so far reported² between these are in the specific optical rotation and alcohol solubility of their calcium salts. Orr³ found that chondroitin sulphate from cartilage gives an infra-red spectrum which suggests that the product is a mixture of two isomers, *A* and *B* (see below). By counter-current electrophoresis he was able to obtain the faster component of this mixture, which exhibited in the 700-1,000 cm^{-1} region 3 bands, at 928, 855 and 725 cm^{-1} , respectively, and was called the *A* isomer. The *B* isomer, on the other hand, was isolated alone in a well-defined form from the nucleus pulposus and showed two bands at 825 and 775 cm^{-1} , respectively. Meyer *et al.*² pointed out the similarity between Orr's *B* isomer and chondroitin sulphate *C*. On the other hand, both *A* types show the same optical rotation and origin. The following results seem to give a different picture of the mucopolysaccharides of cartilage and nucleus pulposus.

Extracts of (a) cartilage from horse nasal septum and (b) nucleus pulposus from human intervertebral disk were made using aqueous solutions of 30 per cent potassium chloride and 1 per cent potassium carbonate⁴.

These were centrifuged, and the resulting solutions were dialysed. The retained soluble fractions were then precipitated with potassium acetate and alcohol at 0° C. The precipitates so obtained were purified by application of this technique three times; finally, the resulting specimens were dried with absolute alcohol and ether.

A preliminary paper electrophoresis of our preparations *MC* (from cartilage) and *MP* (from nucleus pulposus) showed the same main features, that is, two components were present and both stained meta-chromatically with toluidine blue. One component was stationary and the second one mobile and negatively charged. A previous investigation⁵ showed that in *MC* the first component was mucoprotein, the second one being chondroitin sulphate. By analogy, the immobile component of *MP* was thought to be a protein-polysaccharide complex, the mobile one a mucopolysaccharide. The amino-acid composition of *MP* was shown, by paper chromatography, to be similar to that of *MC*, already reported elsewhere⁵.

An infra-red investigation gave the following results. Both *MC* and *MP* showed the spectrum of Orr's *A* isomer. *MC* was repeatedly treated with kieselguhr to give a mucopolysaccharide free from mucoprotein which showed an *A*-type spectrum (Fig. 1). The same infra-red spectrum was obtained from a crystalline calcium chondroitin sulphate⁶ (which is a mixture of chondroitin sulphates *A* and *C*, following Meyer's criteria), and a preparation obtained by deproteinizing a mucoprotein from cartilage⁷. Therefore, we suggest that only one type of chondroitin sulphate is present in cartilage. This appears to confirm Meyer's hypothesis² that chondroitin sulphates *A* and *C* are only two fractions of the same polydisperse substance.

By treatment of *MP* with kieselguhr we obtained a free mucopolysaccharide which showed the *B* isomer spectrum (Fig. 2). Using paper chromatography and analytical methods, this mucopoly-

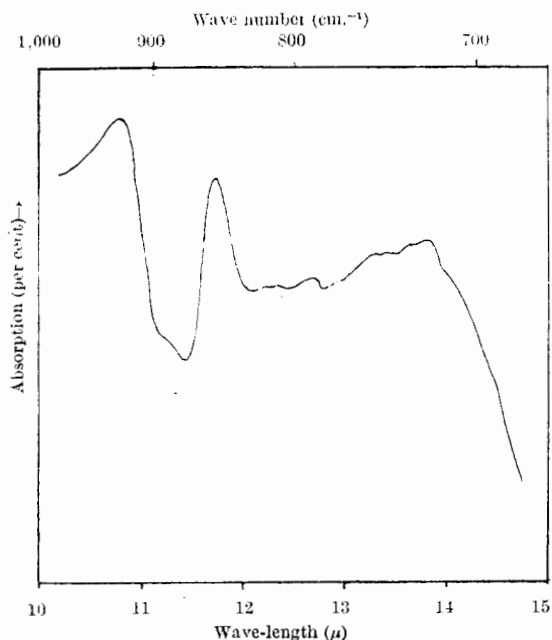


Fig. 1. Infra-red spectrum of chondroitin sulphate

saccharide was identified as keratosulphate (in agreement with a previous finding on a similar preparation⁸). It is reasonable to conclude, therefore, that *MP* is a mixture of a mucoprotein the carbohydrate component of which is chondroitin sulphate and a free mucopolysaccharide, keratosulphate. We cannot, however, exclude the presence as minor constituents of keratosulphate in mucoprotein or of chondroitin sulphate in the mobile component of *MP*. The lower intensity of the $1,736\text{ cm.}^{-1}$ band in comparison with that at $1,560\text{ cm.}^{-1}$ found by Orr in the *B* type as compared to the *A* type (attributed by him to a lower hexuronic acid : hexosamine ratio) is in agreement with our conclusions.

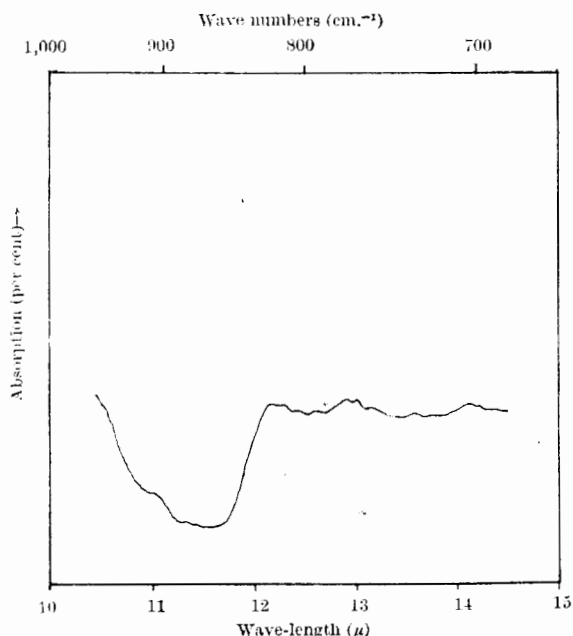


Fig. 2. Infra-red spectrum of keratosulphate

A more detailed presentation of this work will be given elsewhere in due course.

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Excitation of Molecular Spectra by Shock Waves

SEVERAL spectroscopic studies have recently been made of the light emitted from gases submitted to an intense shock wave¹⁻³, but little information is available about the emission from air and other permanent gases. The very high temperatures available make the shock tube a convenient device for study of spectra of astrophysical interest, and a knowledge of the spectrum of air is necessary in any consideration of its high-temperature emissivity which may be required for problems of supersonic flight at high altitude. We have studied emission from air, nitrogen, oxygen, carbon monoxide and carbon dioxide or mixtures of these with argon.

The shock tube, 5 ft. long and $2\frac{1}{2}$ in. in diameter, is of copper, as this has a simple spectrum which does not interfere with that of the gas being studied. The emission was studied through quartz side-windows. For examination of the primary shock wave, a dump chamber was used for preventing its reflexion, while for the hotter reflected shock an end-plug was inserted close to the windows. Other features were similar to those used by Fairbairn and Gaydon³. Spectra were recorded photographically with a small $f/4$ 'Hilger' Raman spectrograph. Comparison of the variation in time of light emission of two spectrum lines was made by using two spectrometers set to view the same point of the shock from opposite sides: the spectrometers were fitted with photomultipliers, connected to a 'Cossor' 1038 double-beam oscillograph.

Strong reflected shocks through pure argon (99.8 per cent) give intense light emission⁴, the spectrum showing argon lines superposed on a continuum