



Fig. 2. Abdruckfilm aus Polyamid des Hexamethyldiamins mit Sebacinssäure. (100) KCl. (Aufnahme: E. W. FISCHER)

Maschen des von den Fibrillen gebildeten Netzes ist eine Struktur analogie zwischen der Verwachsungsfläche von Wirtskristall und Polyamidfibrille massgebend. Dabei dürfte auf Grund der auf dem Gebiet der Epitaxie im niedermolekularen Bereich vorliegenden Erfahrung eine eindimensionale Struktur analogie zwischen Polyamid und Matrize bereits hinreichend sein.

Als Verknüpfungsstellen des Polyamids mit den Verknüpfungsstellen der Matrize (zum Beispiel Ionen der Alkalihalogenide oder Dipolen des Rohrzuckers) werden in erster Linie dessen polare Amidgruppen in Frage kommen; dabei wird besonders die Ausbildung von Wasserstoffbrücken in Betracht zu ziehen sein. BERNAL⁵ hat am Beispiel der Orientierung des Polyäthylenmole-

küls auf NaCl darauf hingewiesen, dass hierbei auch eine gewisse Streckung (Entfaltung) des Makromoleküls eintritt.

II. Bekanntlich wird eine Reihe von Erscheinungen biologisch spezifischer Aktivität auf Abdruckvorgänge unter Mitwirkung von hochmolekularen Polyamiden, nämlich Proteinen, zurückgeführt; als besonders eindrucksvolles Beispiel sei hier nur die Antikörperbildung genannt. Die von PAULING⁶ vertretene Theorie der Antikörperbildung geht von der von BREINL und HAUROWITZ⁷ entwickelten Vorstellung aus, dass Antikörper und Antigen eine komplementäre Struktur besitzen. Zu den Einzelheiten dieser Theorie sei auf die einschlägige Literatur verwiesen⁸. Nach dieser Vorstellung werden die antigenen Bezirke an der Oberfläche der natürlichen Antigene ebenso wie die determinanten Gruppen der künstlichen Antigene, zum Beispiel Azoprotein, von dem Antikörper bildenden Polyamidmolekül, das heisst dem Globulinmolekül, räumlich umhüllt, so dass sich ein taschenförmiger, räumlicher, negativer Abdruck bildet.

Der experimentelle Nachweis, dass Polyamide charakteristische netzförmige flächenhafte Abdrücke von atomaren oder auch molekularen Anordnungen zu bilden vermögen, wirft die Frage auf, ob diese Abdrücke als Modelle für die Antikörperbildung angesehen werden können. Als verknüpfende Stellen des Antigens bieten sich in erster Linie die polaren Gruppen der antigenen Bezirke der natürlichen Antigene und die determinanten Gruppen einschliesslich der damit verbundenen Tyrosin- und Histidinreste der künstlichen Antigene an.

Einzelheiten zu der Vorstellung über die Entstehung von Antikörpern durch Bildung von flächenhaften Abdrücken der massgebenden Stelle der Antigenoberflächen durch das Protein des Antikörpers im Wege der orientierten Verwachsung (Epitaxie) werden an anderer Stelle veröffentlicht.

Summary. The macromolecules of high molecular polyamide films obtained in contact with (100) of KCl, KBr, and sucrose as a matrix are oriented by overgrowth in the form of a characteristic network of fibrils. This network formation of polyamides in contact with the atomic arrangement in crystal lattice planes as a matrix is proposed as a model for antibody formation.

J. WILLEMS

Krefeld (Deutschland), Tiergartenstrasse 21, 15. Mai 1961.

⁵ J. D. BERNAL, Faraday Soc. Discuss. 1958, Nr. 25, 12.

⁶ L. PAULING, J. Amer. chem. Soc. 62, 2643 (1940).

⁷ F. BREINL und F. HAUROWITZ, Z. physiol. Chem. 192, 45 (1930).

⁸ Vgl. aus neuester Zeit z.B. die zusammenfassende Darstellung von F. HAUROWITZ, Z. angew. Chem. 73, 153 (1961).

Sulfur Exchange Between Thiotaaurine and Hypotaaurine

In a previous paper, spontaneous transulfuration between thiotaaurine and cysteinesulfinic acid, and between alaninethiosulfonic acid and hypotaaurine, has been reported¹.

We now present some data supporting a similar reaction between thiotaaurine and hypotaaurine, obtained by the use of labelled compounds.

³⁵S-thiotaaurine and hypotaaurine were prepared enzymically by the following procedure. Labelled cysteamine and elementary sulfur were incubated with an enzyme

preparation from hog kidney, precipitated between 20 and 60% ammonium sulfate saturation, under the experimental conditions reported elsewhere². The enzyme produces hypotaaurine and thiotaaurine from thiocysteamine formed from the combination of cysteamine with elementary sulfur². The reaction mixture was chromatographed in phenol, labelled thiotaaurine and hypotaaurine were localized in the chromatogram by radio-scanning

¹ C. DE MARCO and M. COLETTA, Exper. 16, 534 (1960).

² D. CAVALLINI, C. DE MARCO, and B. MONDOVI, Enzymologia 23, 101 (1961).

and eluted separately in a minimum amount of 0.01 *M* phosphate buffer pH 7.4. The eluates from several chromatographic strips were combined to obtain sufficient amounts of labelled compounds.

A 10^{-3} *M* solution of pure thiotaurine³ was added with labelled thiotaurine: 0.5 ml of this solution were chromatographed in phenol, and the strip was scanned for radioactivity by passing it under the mica window of a Geiger counter, protected by a lead shield with a 1.5 cm long window: 1.5 cm long portions of the strip were counted for 1 min each (Figure a).

The same solution was then made 10^{-3} or $3 \cdot 10^{-3}$ *M* in respect to hypotaurine, and, after 15 min standing, 0.5 ml were chromatographed, and scanned quantitatively for radioactivity (Figure b, c).

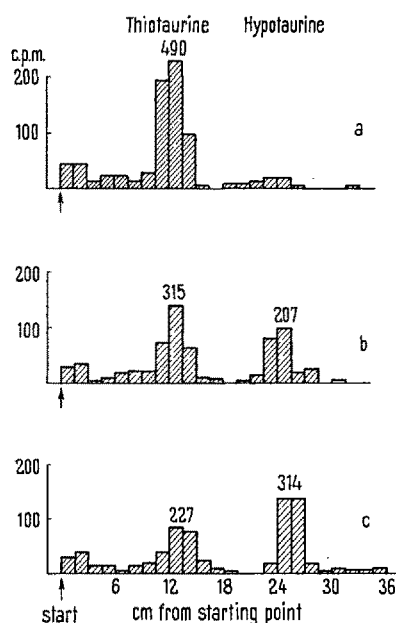
The procedure was repeated with a 10^{-3} *M* solution of pure hypotaurine⁴ labelled by the addition of ³⁵S hypotaurine and then added with thiotaurine.

These experiments show that radioactivity passed from labelled thiotaurine to hypotaurine and *vice versa*, and demonstrate the occurrence of a readily spontaneous transulfuration reaction.

This reaction, like those described previously, is of some interest also from a technical point of view. Transulfuration could in fact be responsible for the appearance in radiochromatograms of unexpected radioactive spots upon addition of unlabelled compounds.

Finally, the above results clearly demonstrate that spontaneous transulfuration between compounds of the *R*-SO₂-SH and *R*-SO₂H type is a general reaction for compounds in which *R* is either a HOOC-CHNH₂CH₂- or a H₂N-CH₂-CH₂-residue.

Résumé. Les auteurs ont préparé avec une enzyme de la thiotaurine et de l'hypotaurine marquées par le et S³⁵ ont démontré que ces deux composés peuvent échanger spontanément un atome de soufre en se transformant l'un dans l'autre.



Unidimensional chromatograms developed in phenol of: (a) labelled thiotaurine; (b) labelled thiotaurine (final concentration 10^{-3} *M*) added with unlabelled hypotaurine (final concentration 10^{-3} *M*); (c) labelled thiotaurine (final concentration 10^{-3} *M*) added with unlabelled hypotaurine (final concentration $3 \cdot 10^{-3}$ *M*).

C. DE MARCO and L. TENTORI

Istituto di Chimica Biologica dell'Università di Roma e Istituto Superiore di Sanità, Roma (Italy), April 28, 1961.

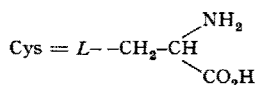
³ D. CAVALLINI, C. DE MARCO, and B. MONDOVI, *Bull. Soc. Chim. biol.* **40**, 711 (1958).

⁴ D. CAVALLINI, C. DE MARCO, B. MONDOVI, and F. STIRPE, *R. Accad. Naz. Lincei* **18**, 552 (1955).

'Cystine Monosulfoxide' and Related Compounds

The oxidation states which are intermediate between cystine (I) and cysteic acid (VII) are of considerable interest in studies of the metabolism of cystine¹ and the oxidation of cystine residues in proteins^{2,3}. Until recently only two of the possible intermediate oxidation products had been synthesized; the thiolsulfonate (III)⁴⁻⁶ and the sulfinic acid (VI)⁷. Syntheses have been reported of the corresponding thiolsulfinate (II)^{4,8,9}, disulfone (IV)¹⁰ and sulfenic acid (V)¹¹, some of which were unstable, but as these products had variable compositions, they were probably mixtures. Last year in this journal¹² a new synthesis of the 'monosulfoxide' (II) was described, whereby III was reduced with HI to give a stable product.

- I Cys-S-S-Cys
- II Cys-S-SO-Cys
- III Cys-S-SO₂-Cys
- IV Cys-SO₂-SO₂-Cys
- V Cys-SOH
- VI Cys-SO₂H
- VII Cys-SO₃H



This preparation¹² has been repeated. However, when the product is examined by paper electrophoresis in 10% acetic acid, or better paper electrophoresis followed by paper chromatography in the transverse direction¹³, it is found to be a mixture of (I) and (III). On polarographic reduction in 0.1 *N* HCl solution at the dropping mercury

cathode, the 'monosulfoxide' gives a complex wave with inflections at -0.18 *V* and -0.45 *V* (versus the saturated calomel electrode). Under the same conditions and in the same voltage range III and I give simple waves with half-wave potentials at -0.18 *V* and -0.45 *V* respectively, again suggesting that the 'monosulfoxide' product is a

¹ L. YOUNG and G. A. MAW, *The Metabolism of Sulphur Compounds*, Chapter V (Methuen, London 1958).

² J. A. MACLAREN, S. J. LEACH, and I. J. O'DONNELL, *Biochim. biophys. Acta* **35**, 280 (1959).

³ J. A. MACLAREN, S. J. LEACH, and J. M. SWAN, *J. Text. Inst.* **51**, T665 (1960).

⁴ G. TOENNIES and T. F. LAVINE, *J. biol. Chem.* **113**, 571 (1936).

⁵ R. EMILLIOZI and L. PICHAT, *Bull. Soc. chim. Fr.* **1959**, 1887.

⁶ B. J. SWEETMAN, *Nature (Lond.)* **183**, 744 (1959) has shown that this substance has the thiolsulfonate structure (III) and not the 'disulfoxide' structure of TOENNIES and LAVINE⁴.

⁷ T. F. LAVINE, *J. biol. Chem.* **113**, 583 (1936).

⁸ G. TOENNIES, *J. Amer. chem. Soc.* **56**, 2198 (1934).

⁹ H. GRÄFJE, *Diplomarbeit Giessen* (1955) and private communication.

¹⁰ G. TOENNIES and T. F. LAVINE, *J. biol. Chem.* **105**, 107 (1934).

¹¹ G. TOENNIES, *J. biol. Chem.* **122**, 27 (1937-1938).

¹² G. E. UTZINGER, *Exper.* **16**, 136 (1960).

¹³ This combination of techniques was suggested by Dr. W. E. SAVIGE of this laboratory. The solvent used was the mixture 'P' of T. L. HARDY, D. O. HOLLAND, and J. H. C. NAYLOR, *Analyt. Chem.* **27**, 971 (1955).