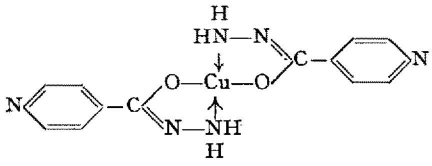
Aus den Versuchen, die zur Ermittlung der Beständigkeitskonstanten dieses Komplexes bei pH 4 durchgeführt wurden, geht hervor, dass die Beständigkeit in der Grössenordnung der Beständigkeit des Oxin-Cu-Komplexes[1] entspricht.



(I)

Ausführliche Angaben über Messungen und Berechnungen erfolgen in einer späteren Mitteilung in den Helv. chim. Acta.

S. FALLAB und H. ERLENMEYER

Anstalt für anorganische Chemie der Universität Basel, 29. Juni 1952.

Summary

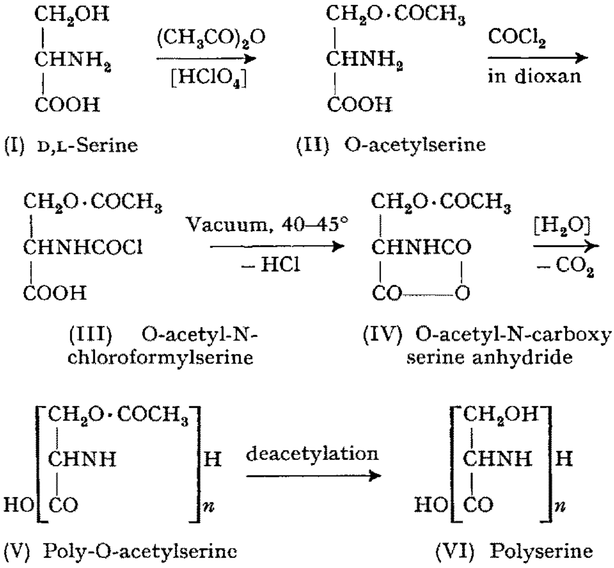
The complex formation between Isonicotinic acid hydrazide and Cu^{++} in aqueous solution has been investigated by a spectrophotometric method.

[1] S. D. RUBBO, A. ALBERT und M. I. GIBSON, Brit. J. exp. Path. *31*, 425 (1950).

Synthesis of Poly-O-acetylserine and of Polyserine

In a previous publication we have reported on the preparation of the N-carboxy anhydrides of O-acetylserine and of O-carbobenzoxyserine[1], starting from O-acetyl-N-carbobenzyloxyserine, and from O,N-dicarbobenzyloxyserine respectively. With the aid of these compounds, polyacetylserine and polyserine are in principle accessible, but the fact that the polymerisation products obtained were of comparatively short chain length, and the interference of certain preparative difficulties, made it desirable to work out a different route for the synthesis of polyacetylserine and of polyserine.

The following scheme represents the steps involved in it:



(I) D,L-Serine

(II) O-acetylserine

(III) O-acetyl-N-chloroformylserine

(IV) O-acetyl-N-carboxyserine anhydride

(V) Poly-O-acetylserine

(VI) Polyserine

The differential acetylation of the hydroxyl group of D,L-serine, leading to O-acetylserine, is possible according to the technique of SAKAMI and TOENNIES[1] under the influence of perchloric acid, making use of the fact that in acetylation with acetic acid anhydride in glacial acetic acid, the acetylation of α-amino groups is increasingly suppressed, while that of the hydroxyl group is promoted catalytically with increasing concentration of perchloric acid.

On suspending the finely powdered O-acetylserine (II) in dry dioxan and passing gaseous phosgene with stirring through the suspension at a temperature of 35–40°, the acetylserine dissolved within about two hours. Removal of excess phosgene and of solvent in vacuo and subsequent heating in vacuo at 40 to 45°, leads directly to O-acetyl-N-carboxyserine anhydride (IV), through loss of hydrogen chloride from the intermediate O-acetyl-N-chloroformylserine (III). A similar procedure has been used by several authors for the preparation of other N-carboxy anhydrides of α-amino acids ("Leuchs" anhydrides[2]). The polymerization was carried out either by heating near the decomposition point of (IV) in high vacuum, or in indifferent solvents (pyridine, dioxan, nitrobenzene), mostly with the addition of initiators. Water, sodium hydroxide or glycine dimethyl amide were used as such.

The poly-O-acetylserine (V) thus obtained was soluble in hot glacial acetic acid and was precipitated from this solution by dry ether. Biuret and ninhydrin reactions were positive. According to analyses the average chain length was about fifty units. In order to obtain polyserine (VI) from polyacetylserine, experiments on deacetylation were carried out, using either lithium hydroxide, barium hydroxide or ammonia as saponification agents. Some difficulties were encountered in obtaining complete deacetylation without splitting the polymer peptide chain.

The polyserine preparations eventually obtained, on evaporating their aqueous solutions in vacuo, constituted hard films; polyserine is hygroscopic, easily soluble in water and gives both biuret and ninhydrin reactions. The average chain length was found by analyses to correspond to the parent acetyl derivatives.

M. FRANKEL, M. BREUER, and S. CORDOVA

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel, April 12, 1952.

Zusammenfassung

Eine befriedigende Methode für die Synthese von Polyazetylserin und von Polyserin geht von O-Azetylserin (II) aus, das aus D,L-Serin durch selektive Azetylierung mittels Essigsäureanhydrid in Eisessig unter katalytischer Mitwirkung von Perchlorsäure erhältlich ist[3]. (II) wird in Dioxansuspension durch Phosgen in O-Azetyl-N-chloroformylserin (III) übergeführt, das im Vakuum bei 40 bis 45° Chlorwasserstoff abspaltet und in O-Azetyl-N-carboxyserinanhydrid (IV) übergeht. Polymerisation von (IV), in der Hitze im Hochvakuum oder in inerten Lösungsmitteln unter Zusatz von Initiatoren, liefert Poly-O-azetylserin (V). Die durchschnittliche Ketten-

[1] M. FRANKEL and M. HALMAN, J. Chem. Soc., London (in press).

[1] W. SAKAMI and G. TOENNIES, J. Biol. Chem. *144*, 203 (1942).

[2] F. FUCHS, Ber. Dtsch. chem. Ges. *55*, 2943 (1922). – A. L. LEVY, Nature *165*, 152 (1950). – A. C. FARTHING and R. J. W. REYNOLDS, Nature *165*, 647 (1950) (cf. Patentliterature cited there). – A. C. FARTHING, J. Chem. Soc. 3213 (1950).

[3] W. SAKAMI and G. TOENNIES, J. Biol. Chem. *144*, 203 (1942). FARTHING, J. Chem. Soc. 3213 (1950).

länge entspricht etwa 50 Einheiten. Desazetylierungsversuche wurden mit Lithiumhydroxyd, Bariumhydroxyd und Ammoniak angestellt. Polyserin (VI) wurde als harter Film erhalten. Es ist hygroskopisch, wasserlöslich und zeigt positive Biuret- und Ninhydrinreaktion.

Contribution to the Structure of Granular Chloroplasts

The ultrastructure of chloroplasts is of importance for an understanding of the complicated reactions connected with photosynthesis. Although the grana in the chloroplasts of the higher plants are visible using the light as well as the electron microscope[1], there are still some unsolved problems which concern the structure of these important cell constituents. Three of these may be mentioned:

(a) What is the connection between chloroplast ultrastructure and the characteristic swelling in unphysiological media?

(b) How are the grana which are arranged in layers parallel to the surface of the chloroplasts[2] connected with each other? Is the chloroplast enclosed by a definite membrane?

(c) Is it possible to prove the proposed lamellar structure of the grana?

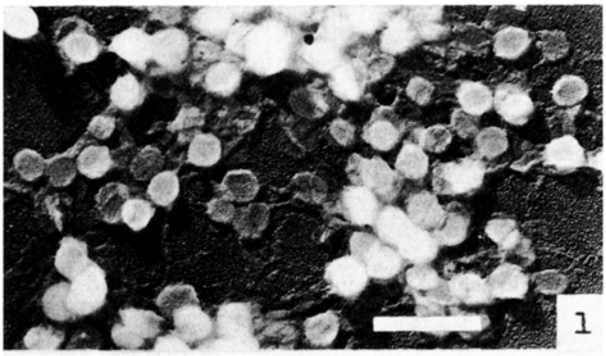
Modern methods of electron microscopy provide a mean to solve certain of these problems.

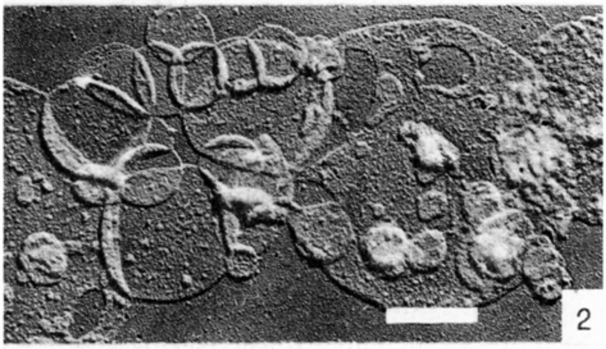
Swelling of Chloroplasts: The fact that different plant species show different patterns of swelling complicates the problem of the ultrastructural basis of swelling.

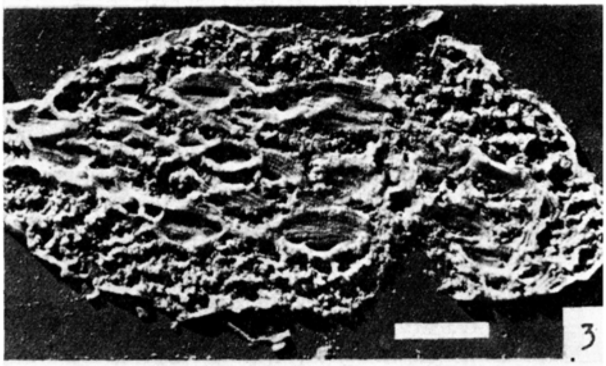
Sometimes the mere contact of chloroplasts with distilled water causes their swelling to structureless blebs of a foamy appearance. Thereby the grana, easily visible in material isolated with phosphate buffer pH 6·4 or sucrose solution (Fig. 1), disappear almost completely (Fig. 2). Spinach chloroplasts are very suitable for studying this phenomenon. Only exceptionally can intact grana be seen in preparations of swollen chloroplasts. We presume from the granular appearance of the surface of the formed blebs that the structural units responsible for the rapid swelling are globular particles. To consider these blebs, even when they are folded, as the remainder of a membrane surrounding the chloroplast, is highly questionable. As yet the existence of such a well defined membrane, suggested by indirect methods, has not been proved.

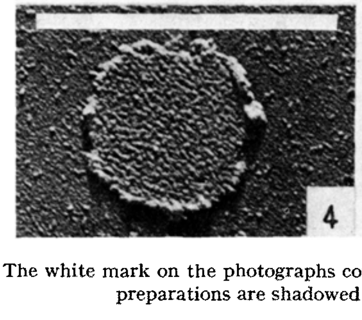
It will be an important task to investigate the connection between the characteristic swelling figures of certain chloroplasts and their ultrastructure. A valuable effort in this direction has been made by STRUGGER[3] using the phase microscope.

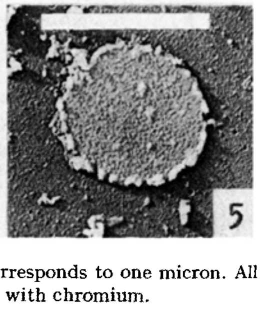
The Ultrastructure of the Grana: The same methods used to investigate the arrangement of the lamellae in the big algal chloroplasts[4] are suitable to inform us about the ultrastructure of the grana whose lamellar composition has already been suggested by experiments with the polarizing microscope[1] and the electron microscope[2].











The white mark on the photographs corresponds to one micron. All preparations are shadowed with chromium.

Fig. 1.–Spinach grana, isolated in phosphate buffer pH 6·4. 14,000:1.
Fig. 2.–Spinach chloroplast, isolated in distilled water. 12,000:1.
Fig. 3.–Section through a tulip chloroplast. Fixation 15 min with 1% OsO_4. 12,000:1.
Fig. 4.–Single circular layer obtained from a tulip chloroplast treated with sonic oscillations. Fixation 25 min with 1% OsO_4. 39,000:1.
Fig. 5.–Single circular layer obtained from an *Aspidistra* chloroplast treated with sonic oscillations. Fixation 17·5 *h* with 1% OsO_4. 22,000:1.

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[1] E. HEITZ, Planta *18*, 617 (1932); *26*, 134 (1936). – J. DOUTRELIGNE, Kon. nederl. Akad. Wetensch. *38*, 886 (1935). – L. ALGERA *et al.*, Biochim. biophys. acta *1*, 517 (1947). – S. GRANICK and K. R. PORTER, Amer. J. Bot. *34*, 545 (1947). – A. FREY-WYSSLING and K. MÜHLETHALER, Vjschr. naturf. Ges. Zürich *97*, 179 (1949).

[2] E. HEITZ, Planta *26*, 134 (1936).

[3] S. STRUGGER, Ber. dtsch. bot. Ges. *64*, 69 (1951).

[4] E. STEINMANN, Exptl. Cell Res. *3*, 367 (1952).

[1] W. MENKE, Protoplasma *21*, 279 (1934).

[2] E. STEINMANN, Exptl. Cell Res. *3*, 367 (1952). – A. FREY-WYSSLING and K. MÜHLETHALER, Vjschr. naturf. Ges. Zürich *97*, 179 (1949).