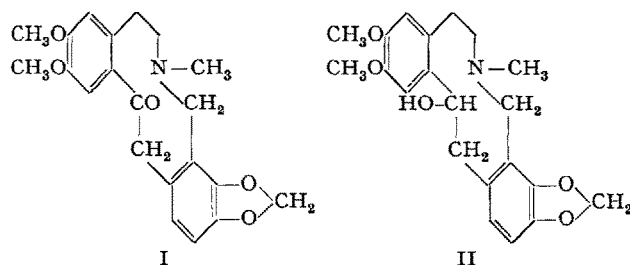


extreme difficulty¹. As lithium aluminium hydride is a specific reagent for reducing ketones to secondary alcohols, its use seemed possible.

On studying the reaction, it was found that dihydrocryptopine is produced in 95% yield. The insolubility of cryptopine in ether, which made the manipulation difficult, was overcome by dissolving the alkaloid in benzene. The ease and quantitative nature of the reaction makes lithium aluminium hydride reduction far the best method for the preparation of dihydrocryptopine.

Experimental. Cryptopine (m.p. 218°, 1 g) was dissolved in benzene (50 ml) and the solution was added through a dropping funnel in about two minutes time to a solution of lithium aluminium hydride (about 100 mg in 50 ml ether). A heavy white precipitate was formed immediately. The mixture was allowed to stand for five minutes and was then hydrolysed with 10 ml of dilute hydrochloric acid. After neutralizing with sodium carbonate the mixture was extracted thrice with 50 ml portions of chloroform. The extracts were combined and dried over magnesium sulphate. On removing the solvent a solid residue was obtained which melted at 186–188°. After one crystallization from benzene it melted sharply at 188–189° and showed no depression in m.p. when mixed with an authentic sample of dihydrocryptopine. The yields were 930–980 mg based on the substance melting at 186–188°.



R. MIRZA

Central Laboratories, Hyderabad, India, February 17, 1952.

Zusammenfassung

Kryptopin lässt sich mit LiAlH_4 in 95%iger Ausbeute zu Dihydrokryptopin reduzieren.

¹ A. PICTET and G. H. KRAMER, Ber. dtsch. chem. Ges. 43, 1333 (1910). – P. W. DANCKWORTT, Arch. Pharm. 250, 590 (1912). – W. H. PERKIN, J. Chem. Soc. 109, 837 (1916).

Relation between Collagen and Mineral Salts in Bone Tissue

In some animal species there is a precipitation of calcium salts in certain tendons. These calcified tendons give an X-ray fibre photograph similar to that of a longitudinal section of a long bone¹. However, there seems to be a more pronounced orientation of the mineral salts in the calcified tendon than in the bone. The orientation is best seen in the 3.4 Å ring. If the mineral salts are in the form of hydroxyapatite, the *c*-axis of the hexagonal crystals is parallel with the fibre axis of the collagen. Therefore it looks as if the collagen *in vivo* in some way orients the mineral salts.

Rat tail tendon was soaked in solutions of different ionic strength where hydroxyapatite was being formed. After drying, these samples were subjected to X-ray diffraction analysis. In specimens where only a small amount of mineral salts had been precipitated in the well oriented collagen, the originally meridional 2.9 Å spacing of collagen continued equatorially but had an equatorial spacing of 2.7–2.8 Å. This ring thus corresponded to the 2.9 Å collagen spacing and the strong 2.76 Å ring from hydroxyapatite. The hydroxyapatite ring at 3.4 Å could be clearly seen although faint in some samples. In a few samples the 3.4 Å ring was slightly more intense meridionally than equatorially. Similar results were obtained if the tendons had been soaked in chondroitin sulfuric acid before they were laid in the solution where hydroxyapatite was being formed. The results therefore tend to indicate that the collagen also had the ability to orient the mineral salts in some of the *in vitro* experiments.

Further experiments are in progress.

A. ENGSTRÖM, B. ENGFELDT, and R. ZETTERSTRÖM

Department for Cell Research Karolinska Institutet, Stockholm, April 2, 1952.

Zusammenfassung

Bei Ablagerung von Hydroxylapatit in kollagenen Fasern des Knochengewebes können diese zur Orientierung der anorganischen Moleküle führen.

Spektrales Verhalten einiger fünfatomiger heterozyklischer Grundkörper in der Schülerschen Entladungsröhre¹

Nach der Methode der Elektronenstossanregung wurden in der Schülerschen Entladungsröhre² mittels Heliums als Trägergas die Emissionsspektren von Furan, Pyrrol, Thiophen, Selenophen und N-Methylpyrrol untersucht. Die Ergebnisse an diesen Stoffen, die einer weitgehenden Reinigung unterworfen worden waren, sind in der Tabelle zusammengestellt. Die Spektren der einfachsten Radikale C_2 , CH , C_2H_2 ,³ NH treten bei tiefen Drucken auf, sie werden mit steigendem Druck allmählich schwächer; die Spektren der das Heteroatom enthaltenden Radikale (CN, CS, CSe) erscheinen ebenfalls bei tiefem Druck, werden aber mit steigendem Druck zuerst stärker, um dann an Intensität wieder abzunehmen; einzig das CO (im Furan) verhält sich anders, indem sein Spektrum schon beim tiefsten Druck sehr stark vorkommt und mit steigendem Druck sehr schnell schwächer wird.

Das aus zwei Heteroatomen gebildete Molekül kann nur beim Selenophen bei relativ hohem Druck nachgewiesen werden; die Ringanregung des unzersetzten Moleküls kommt nur beim N-Methylpyrrol vor. Die Spektren aller untersuchten Stoffe ergeben beim höchsten Druck auch ein Emissionskontinuum im Blaugrün, das bei höherer Temperatur der Rohrwand stärker wird.

¹ Diese Arbeit erscheint ausführlich demnächst in *Gazzetta Chimica Italiana*. Der experimentelle Teil derselben wurde während eines kurzen Aufenthaltes des Verfassers als Gast bei der Forschungsstelle für Spektroskopie in der Max-Planck-Gesellschaft ausgeführt. Herrn Prof. SCHÜLER möchte er auch an dieser Stelle seinen besten Dank für die ihm bereitete freundliche Aufnahme aussprechen.

² H. SCHÜLER, Spectrochimica Acta 4, 85 (1950), dort vorangehende Literatur.

³ H. SCHÜLER und L. REINEBECK, Z. Naturforsch. [A] 7 (1952), im Druck.

¹ A. ENGSTRÖM and R. ZETTERSTRÖM, Exp. Cell Res. 2, 268 (1951).