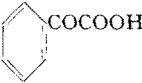
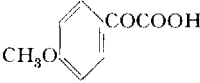
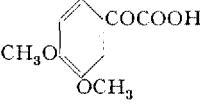
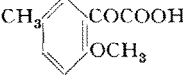
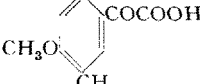
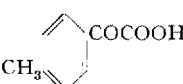
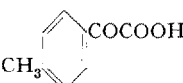
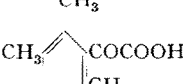
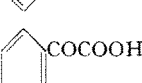


Acid	Dissociation Constant K	pK	Polarographic pK	Recombination $k \text{ mol}^{-1} \text{ s}^{-1}$	Droptime $t \text{ s}$	Dissociation k' $\text{l}^1 \text{ mol}^{-1} \text{ s}^{-1}$
	4.07×10^{-2}	1.39	6.81	3.58×10^{11}	4.1	1.46×10^{10}
	2.25×10^{-2}	1.65	6.78	1.24×10^{11}	3.5	2.77×10^9
	1.63×10^{-2}	1.79	7.52	4.13×10^{12}	3.64	6.70×10^{10}
	2.4×10^{-2}	1.62	6.92	4.42×10^{11}	3.64	1.06×10^{10}
	1.66×10^{-2}	1.78	7.05	4.85×10^{11}	3.64	8.06×10^9
	3.0×10^{-2}	1.52	6.80	2.79×10^{11}	3.64	8.44×10^9
	4.4×10^{-2}	1.36	6.96	8.44×10^{11}	3.64	3.68×10^{10}
	3.55×10^{-2}	1.45	7.26	2.73×10^{12}	3.64	9.68×10^{10}
 in D_2O	1.59×10^{-2}	1.79	6.69	7.65×10^{10}	4.40	1.24×10^9

Plotting $\log k$ against σ for the para-substituted acids and for the unsubstituted acid we obtain a straight line the gradient of which gives $\rho = 1.43$.

MARY S. WHEATLEY

Chemistry Laboratory, University of New Brunswick,
Fredericton, N. B., March 19, 1956.

Zusammenfassung

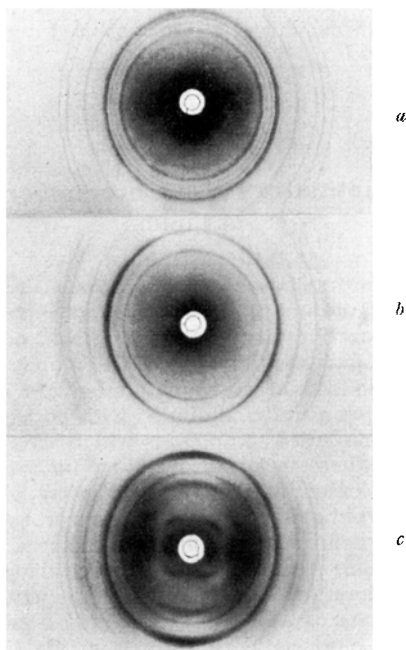
Die Rekombinationsgeschwindigkeit von Phenylglyoxylationen und Hydroniumionen wird aufs neue in neutraler Lösung bestimmt, und es wird gezeigt, dass sie dem Wert, der von uns früher in alkalischer Lösung gefunden wurde, entspricht. Beide Werte stimmen auch mit den Literaturangaben überein.
Die Rekombinationsgeschwindigkeiten einer Serie von substituierten Phenylglyoxylsäuren und die Rekombinationsgeschwindigkeit von Phenylglyoxylat- und Deuteroniumionen werden angegeben.

In Vitro Calcification of Collagen

We have found that under suitable conditions it is possible to obtain calcium phosphate inside collagen fibres in the form of hydroxyapatite. This was observed in the course of a series of studies undertaken in continuation of the observations on the oriented crystallization of soluble inorganic salts in collagen¹. Several insoluble compounds like silver oxide, white lead, calcium fluoride and calcium carbonate could be crystallized inside collagen fibres by keeping them in solutions containing suitable concentrations of the required ions. Attempts were then made to precipitate calcium phosphate from Ringer solution, mixtures of mono- and disodium phosphate solutions with calcium chloride solution and small variations of these, but they were not successful. Sometimes calcium carbonate or calcium orthophosphate dihydrate crystallized in the collagen but only slightly. However, if collagen fibres are kept in a water suspension of precipitated calcium phosphate (B.D.H.) then an excellent precipitation of hydroxyapa-

¹ G. N. RAMACHANDRAN and G. K. AMBADY, *Exper.* 11, 343 (1955).

tite inside the collagen is obtained. It may be mentioned that the fibre was kept in the supernatant solution over the solid calcium phosphate and that the specimen was unchanged on washing with distilled water. The X-ray diffraction pattern of a typical specimen, together with the pattern given by a bone specimen, are shown in the Figure (a) and (b). The resemblance between the two is striking but for the greater sharpness of the lines observed in the synthetic specimen, showing that the particle size of the hydroxyapatite crystals is much larger.



HENDRICKS² has suggested that, in bone, carbonate and citrate ions occur essentially on the surface of the hydroxyapatite crystals and that their occurrence limits the particle size. Consequently experiments were made by (a) passing carbon dioxide continuously through the suspension of calcium phosphate and (b) adding citric acid to it. The former had practically no effect on the particle size, while the latter definitely decreased the particle size at very low concentrations. The optimum condition was obtained by adding 0.02 mg/ml of citric acid with the pH of the solution adjusted to 7.6 by addition of 10% ammonium hydroxide. The X-ray diffraction pattern of a specimen obtained with this solution is shown in the Figure (c) and the very close correspondence to the bone pattern is noteworthy. Thus the synthetic formation of a material very similar to bone from collagen appears to have been achieved.

A number of other observations have also been made, such as the inhibiting effect of certain ions and the relative deposition of calcium phosphate and other salts when both are present. These details will be published elsewhere in due course. This appears to be the first time that the deposition of hydroxyapatite on collagen fibres as such has been obtained. Previous studies on the

calcification of cartilage have invariably been made only with collagenous tissue.

G. N. RAMACHANDRAN and M. S. SANTHANAM

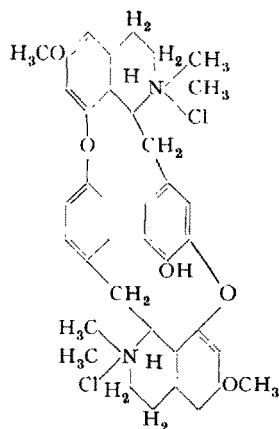
Department of Physics, University of Madras, India,
June 1, 1956.

Zusammenfassung

In Collagenfasern kann durch Aufbewahren in einer wässrigen Suspension von gefällttem Kalziumphosphat eine Ablagerung von Hydroxyapatit erhalten werden. Der Niederschlag lässt sich durch Waschen mit Wasser nicht entfernen. Das Röntgenbild der Abscheidung gleicht weitgehend demjenigen des anorganischen Bestandteils der Knochen. Nach Zufügung einer Spur Zitronensäure ist auch die Teilchengröße von derselben Ordnung wie im Knochen.

Wirkung von δ -Tubocurarinchlorid auf den O_2 -Verbrauch der Eier von *Psammecinus microtuberculatus*

Es wurde der Einfluss von δ -Tubocurarinchlorid (dTC)¹ auf den Stoffwechsel von Seeigeleiern studiert.



δ -Tubocurarinchlorid

Die Untersuchungen wurden im Mai 1956 in Neapel an befruchteten und unbefruchteten Eiern von *Psammecinus microtuberculatus* durchgeführt. Anwendung fand die direkte Messmethode nach Warburg mit CO_2 -Absorption durch 12prozentige KOH: im Atmungsraum 3 cm³ 5% Eisuspension in Golfwasser, Versuchstemperatur 21°, Schüttelgeschwindigkeit 90 Einzelschläge min⁻¹, Exkursion 5 cm, Gasphase Luft, Bestimmung der Stoffwechselgrößen über 2–3 h in 20-Minuten-Abständen nach Umrechnung auf Grundbedingung mit der Warburgschen Formel für die Gefässkonstante und graphische Darstellung der Q_{O_2} -Einzelwerte in einem Koordinatensystem nach der Zeit.

Die Untersuchungen haben ergeben, dass dTC in Konzentrationen über 1,2 mg% den O_2 -Verbrauch von Seeigeleiern signifikant senkt. Dieser Effekt lässt sich sowohl an befruchteten als auch an unbefruchteten

² S. B. HENDRICKS and W. L. HILL, *Metabolic Interrelations*, Transactions of the Third Conference of Macy Foundation (New York 1951), p. 173.

¹ H. KING und K. FOLKERS, *Science* 97, 467 (1943).