clear solution two volumes of acetone are added. The precipitate is filtered and the precipitate is washed with 200 ml of acetone and 200 ml of ether. Yield 30–40 g.

The enzyme preparation is dissolved by shaking for 30 minutes in distilled water immediately before use. The rate of hydrolysis is shown in Fig. 1. It is evident from the figure that the D-ester is stable against the pancreatic enzymes for at least 72 hours and that, with the amount of enzymes used, practically all the L-ester is hydrolyzed after 24 hours. The fact that hydrolysis with enzymes is asymmetrical is shown by the method for the preparation of D-valine described in the following. The investigations showed that, under similar experimental conditions, the isobutyl ester of DL-valine is also hydrolyzed to some extent with water.

Preparation of D-valine. — 100 g of the isobutyl ester of DL-valine are shaken for 48 hours with 400 ml of a 5 per cent solution of pancreatic enzymes at room temperature. 400 ml of ether and 20 ml of concentrated ammonia are added to the mixture. The ether layer is separated and the aqueous solution extracted twice more, each time with 100 ml of ether. The ether extracts are dried over sodium sulfate and the ether evaporated after the sodium sulfate has been removed. The remaining oil is shaken for 48 hours at room temperature with 100 ml of 5 per cent pancreatic enzyme solution. While stirring 100 ml of ether and 5 ml of concentrated ammonia are added to the digestion mixture. The ether layer is separated and the aqueous solution extracted twice more, each time with 100 ml of ether. The ether extracts are dried over sodium sulfate. The sodium sulfate is removed and the ether is evaporated. The oil of the isobutyl ester of D-valine thus obtained is refluxed for 12 hours with 350 ml of 20 per cent hydrochloric acid. The solution is evaporated *in vacuo* to dryness and for a second time after adding 100 ml of water. The hydrochloride of D-valine thus obtained is dissolved in 200 ml of 96 per cent alcohol. 50 ml of pyridine are added and the mixture is placed overnight in the refrigerator. The precipitate is filtered off and washed with 50 ml of alcohol and 50 ml of ether. The impure D-valine is recrystallized by dissolving in hot water (11 ml per g), decolorized with 0.5 g of norit and the clear solution treated with an equal volume of 95 per cent alcohol. The precipitate is washed with absolute alcohol and ether as described. To obtain an analytically pure sample, the D-valine is again recrystallized and washed as outlined above. The product thus obtained weighs 14–16 g (41 to 47 per

cent of theory). Analysis of the D-valine obtained with this method gave the following results:

$C_5H_{11}O_2N$ Calculated, N 11.96; found, N 11.95
 $\alpha_D^{23} = -28.2$ to -28.6° ($c = 2$, in 6 N hydrochloric acid).

The figures given in the literature are -29.0° (Fischer¹), -27.1° (Price, Gilbert and Greenstein⁵) and -27.6° (Ehrlich and Wendel⁶) respectively.

1. Fischer, E. *Ber.* **39** (1906) 2320.
2. Holmes, D. F., and Adams, R. *J. Am. Chem. Soc.* **56** (1934) 2093.
3. Duschinsky, R., and Jeannerat, J. *Compt. rend.* **208** (1939) 1359.
4. Ehrlich, F. *Biochem. Z.* **1** (1906) 8.
5. Price, V. E., Gilbert, J. B., and Greenstein, J. P. *J. Biol. Chem.* **179** (1949) 1169.
6. Ehrlich, F., and Wendel, A. *Biochem. Z.* **8** (1908) 399.
7. Warburg, O. *Z. physiol. Chem.* **48** (1906) 205.
8. Brenner, M., and Kocher, V. *Helv. Chim. Acta* **32** (1949) 333.
9. Wretling, K. A. J. *Acta Physiol. Scand.* **20** (1950) 1.
10. Wretling, K. A. J. *J. Biol. Chem.* **186** (1950) 221.
11. Brenner, M., Sailer, E., and Kocher, E. *Helv. Chim. Acta* **31** (1948) 1908.
12. Waldschmidt-Leitz, E. *Z. physiol. Chem.* **132** (1923) 181.
12. Willstätter, R., and Waldschmidt-Leitz, E. *Z. physiol. Chem.* **125** (1923) 150.

Received March 15, 1952.

On the Alleged Complexity of Sodium in Polyhexametaphosphate

BERNHARD ANDERSEN and
KIRSTEN LEHMANN

Laboratory of Zoophysiology, University of
Copenhagen, Copenhagen, Denmark

According to Lamm and Malmgren¹ the Na in $K_2Na_4(PO_3)_6$ is bound in complex form. That is, they state that they have dialyzed a solution of the polyhexametaphosphate (PMP) against 0.1 N HCl, and found that only K exchanges with

H. We have not been able to confirm this in the experiments given below.

PMP was prepared according to Tammann²: 1 equivalent of KH_2PO_4 was heated for 20 minutes to a glowing red. It made no difference whether it was heated to respectively 650°, 750° or 950° C. The resulting KPO_3 was pulverized and treated with a concentrated NaCl solution which contained 2 equivalents of NaCl. The pulverized material swelled and formed a highly viscous and elastic mass which was dissolved in water and freed from the unreacted remainder of KPO_3 by filtration. The PMP was precipitated twice with alcohol and freed from Cl^- by triturating with 50 % alcohol. The composition of the compound agreed with the formula $\text{K}_2\text{Na}_4(\text{PO}_3)_6$. Na and K were determined in the flame spectrophotometer and P was determined according to Fiske and Subbarow⁴.

The characteristics of PMP described by Tammann have been confirmed by us with the exception of conductance which we have not repeated.

The following tests were made:

1. PMP was dissolved in water and precipitated twice with KCl. Flame spectrometry showed that all the Na was replaced by K.

2. PMP was dissolved in 0.1 N HCl and ultrafiltered through cellophane dialyzing tubes³. The ultrafiltrate contained Na as well as K (see Table 1).

3. In order to be sure that the presence of Na in the above mentioned ultrafiltrate was not caused by hydrolysis the following experiment was made. A PMP solution was so prepared by the addition of KCl that $C_{\text{Na}} \sim C_{\text{K}}$. This solution was ultrafiltered and Na and K were found in the filtrate in equal amounts. The appearance of Na in the filtrate was not due to the fact that the dialyzing tubes were permeable to PMP, as analysis of the filtrate showed that there was absolutely no phosphate present.

Table 1. Flame spectrometry of Na and K in the ultrafiltrate of $\text{K}_2\text{Na}_4(\text{PO}_3)_6$ solution with added HCl and KCl.

Exprt. nr.	KH_2PO_4 heated to	Sub- stance added to PMP solution	Found $C_{\text{Na}}/C_{\text{K}}$ in ultrafilt.	$C_{\text{Na}}/C_{\text{K}}$ in liq. residue
III	650°	HCl giving $C_{\text{H}} = 0.1$	1.98	2.26
II		KCl giving $C_{\text{K}} \sim C_{\text{Na}}$	0.88	0.88
IV			1.15	0.76
V	0.51		0.57	
VII	1.09		0.91	
VIII	1.06		1.12	
IX	950°		0.60	0.96
X			0.70	0.84

According to Lamm and Malmgren it should be expected that $(C_{\text{Na}}/C_{\text{K}})$ filtrate = 0 in all experiments.

4. A known amount of PMP was precipitated with BaCl_2 . The Ba content of the precipitate was determined as BaSO_4 , and the content of phosphate was determined colourimetrically. The composition of the precipitate was found to be $\text{Ba}(\text{PO}_3)_2$. Thus, Ba replaces Na as well as K in the PMP.

The tests performed give no reason for the assumption of complex formation between the Na-ion and the PMP-ion.

1. Lamm, O., and Malmgren, H. *Z. anorg. u. allgem. Chem.* **245** (1940) 106.
2. Tammann, G. *J. prakt. Chem.* **153** (1892) 436.
3. Brandt Rehberg, P. *Acta Physiol. Scand.* **5** (1943) 305.
4. Fiske, C. H., and Subbarow, Y. *J. Biol. Chem.* **66** (1925) 375.

Received April 18, 1952.