

Ca⁺⁺ or Versene. The present enzyme preparations contained only traces of Ca⁺⁺, as measured by flame spectrophotometry (0.02% in trypsin and 0.004% in chymotrypsin).

The activation effects described herein, which were also observed with the corresponding amide substrates, are of smaller magnitude and therefore probably of a different type than those usually associated with metal activation of enzymes.⁶ The suggestion that the binding of these cations by the protein involves a shift of the equilibrium among coexistent forms of varying enzymatic activity³ deserves serious consideration.

Further quantitative studies on trypsin, chymotrypsin and carboxypeptidase are now in progress, and together with the details of the present report, will be published at a later date.

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RECEIVED FEBRUARY 16, 1952

(6) A. L. Lehninger, *Physiol. Rev.*, **30**, 393 (1950).

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THE ENZYMIC FORMATION OF SEDOHEPTULOSE PHOSPHATE FROM PENTOSE PHOSPHATE

Sir:

Sedoheptulose (D-altoheptulose), originally discovered in the *Sedum* plant,¹ has recently been reported to occur as a phosphate ester among the early products of photosynthesis.² The hexosem-nophosphate fraction isolated from yeast also has been found to contain about 2% of a heptulose ester.³ We have now identified sedoheptulose phosphate as a product of pentose phosphate metabolism with purified enzymes of animal origin.

Enzymes in red cells⁴ and in bacteria and yeast⁵ which split pentose phosphate to form triose phosphate have been described. We have purified a similar enzyme about 60-fold from rat liver acetone powder extracts by fractionation with ammonium sulfate, methanol and acetone. The enzyme assay was based on the rate of oxidation of reduced diphosphopyridine nucleotide in the presence of α -glycerophosphate dehydrogenase and triose phosphate isomerase.⁶ The purified preparation contains pentose phosphate isomerase but has greater activity with ribulose-5-phosphate than with ribose-5-phosphate. Neither of these substrates is attacked appreciably by the purified liver enzyme unless a system for the removal of the products is added. In the presence of the purified pentose-splitting enzyme and crystalline muscle aldolase,⁷ there is virtually complete removal of pentose phosphate and a recombination of the fragments to form sedoheptulose phosphate. During this proc-

(1) F. B. LaForge and C. S. Hudson, *J. Biol. Chem.*, **30**, 61 (1917).

(2) A. A. Benson, J. A. Bassham and M. Calvin, *THIS JOURNAL*, **73**, 2970 (1951).

(3) R. Robison, M. S. Macfarlane and A. Tazelaar, *Nature*, **142** 114 (1938).

(4) Z. Dische, *Naturwiss.*, **26**, 252 (1938).

(5) E. Racker in W. D. McElroy and B. Glass, "Phosphorus Metabolism," The John Hopkins Press, Baltimore, Md., 1951, Vol. I, p. 147.

(6) E. Racker, *J. Biol. Chem.*, **167**, 843 (1947).

(7) J. F. Taylor, A. A. Green and G. T. Cori, *ibid.*, **173**, 591 (1948).

ess the absorption band at 670 m μ due to pentose in the orcinol reaction is replaced by a band at about 600 m μ , which is identical with that obtained with sedoheptulose. From 2 moles of pentose phosphate approximately 1 mole of sedoheptulose phosphate and about 0.5 mole of triose phosphate were formed (Table I). No explanation is available for the low yield of triose phosphate. The identification of the triose as dihydroxyacetone was based on paper chromatography with acetone-water mixtures. Sedoheptulose was converted to sedoheptulosan tetrabenzoate⁸ after hydrolysis of the reaction mixture with a purified potato phosphatase.⁹ The derivative melted at 164.5–165°, as did an authentic sample,¹⁰ and the mixed melting point was 163.5–164°. The optical rotation was $\alpha^{20}_D -194^\circ$ ($c = 0.72$ in CHCl₃) compared to $\alpha^{20}_D -195^\circ$ for the authentic derivative.

TABLE I

	STOICHIOMETRY OF PENTOSE PHOSPHATE CONVERSION ^a		
	0 min.	Micromoles 60 min.	Δ
Pentose phosphate	6.26	1.48	-4.78
Sedoheptulose phosphate ^b	0	2.43	+2.43
Triose phosphate ^c	0	1.14	+1.14

^a The reaction mixture contained 0.36 mg. of purified pentose-splitting enzyme and 0.19 mg. of recrystallized muscle aldolase in 1.1 cc. of 0.01 M glycylglycine buffer pH 7.4 containing 0.01 M cysteine. Incubation was at 23°.

^b Calculated from the absorption at 580 m μ in the orcinol pentose method of W. Mejsbaum, *Z. physiol. Chem.*, **258**, 117 (1939). ^c Determined by oxidation of reduced diphosphopyridine nucleotide in the presence of α -glycerophosphate dehydrogenase. Since the latter preparation contains aldolase and triose phosphate isomerase, the determination measures fructose diphosphate and glyceraldehyde-3-phosphate, as well as dihydroxyacetone phosphate.

Heptulose phosphate is also formed on incubation of D-erythrose with hexosediphosphate and aldolase. This observation suggests that sedoheptulose phosphate formation from pentose phosphate proceeds by way of a tetrose, derived from 2 two-carbon fragments from pentose phosphate, which under the influence of aldolase condenses with dihydroxyacetone phosphate to yield sedoheptulose phosphate.

(8) W. T. Haskins, R. M. Hann and C. S. Hudson, *THIS JOURNAL*, in press.

(9) A. Kornberg, unpublished procedure.

(10) Prepared from sedoheptulosan generously supplied by Dr. N. K. Richtmyer.

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RECEIVED MARCH 11, 1952

SURFACE CHEMICAL PROPERTIES OF SOLIDS COATED WITH A MONOLAYER OF PERFLUORODECANOIC ACID¹

Sir:

Attention has been directed recently to the modification of the surface chemical properties of a solid

(1) Taken from a thesis submitted by Fred Schulman in partial fulfillment of the requirements for the degree of Ph.D. at The Division of Chemistry, Graduate School, Georgetown University, Washington, D. C.