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 activity[3] 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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(6) A. L. Lehninger, *Physiol. Rev.*, **30**, 393 (1950).
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THE ENZYMATIC FORMATION OF SEDOHEPTULOSE PHOSPHATE FROM PENTOSE PHOSPHATE

Sir:

Sedoheptulose (D-altroheptulose), 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 hexosemonophosphate 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 cells[4] and in bacteria and yeast[5] 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 process the absorption band at 670 mμ due to pentose in the orcinol reaction is replaced by a band at about 600 mμ, 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 tetrabenzoate[8] 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° (c = 0.72 in $CHCl_3$) compared to $\alpha^{20}D$ −195° for the authentic derivative.

TABLE I

STOICHIOMETRY OF PENTOSE PHOSPHATE CONVERSION[a]

	Micromoles		
	0 min.	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 *p*H 7.4 containing 0.01 *M* cysteine. Incubation was at 23°. [b] Calculated from the absorption at 580 mμ in the orcinol pentose method of W. Mejbaum, 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.

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SURFACE CHEMICAL PROPERTIES OF SOLIDS COATED WITH A MONOLAYER OF PERFLUORODECANOIC ACID[1]

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.

by adsorption of an oriented monolayer of a polar-non-polar compound. Many pure liquids which normally spread on clean surfaces of metals were found at 20° to exhibit large contact angles on the monolayer-covered surface. Thus systematic measurements of the surface tension (γ_{LV}°) and the equilibrium contact angle (θ_E) have permitted the determination of the spreading coefficient ($S_{b/a}$), work of adhesion (W_A), and free energy decrease on immersion (f_{SL}). Reports have been presented of similar studies on several low-energy surfaces including polytetrafluoroethylene (a surface covered primarily by $-CF_2-$ groups),[2] polyethylene (primarily a $-CH_2-$ surface),[3] and monolayers of *n*-octadecylamine adsorbed on platinum (a surface covered with $-CH_3$ groups).[4] In the studies cited, liquids with unusually low surface tensions such as perfluorotributylamine (γ_{LV}° = 16.3 dynes/cm.) spread as a duplex film.

In the present work θ_E was measured for more than ninety diverse pure liquids having surface tensions ranging from over 73 to as low as 13.4 dynes/cm. on surfaces of polished platinum, copper and glass which had been modified by adsorption of a close-packed, oriented monolayer of *n*-perfluorodecanoic acid.

Examples of the remarkably large contact angles encountered are: hexadecane (72°), octane (56°), benzene (58°), ethylene glycol (81°), perfluorotributylamine (26°), hexachlorobutadiene (77°), polymethylsiloxane heptadecamer (62°), carbon disulfide (59°), water (102°), and mercury (152°). No liquid was found for which $\theta_E = 0°$. Comparison of other results[2,3,4] for these same liquids shows that the solid coated with an oriented monolayer of perfluorodecanoic acid is the most non-wettable surface ever reported. The contact angles (θ_{CF_3}) for most liquids in contact with this surface and the contact angles on polytetrafluoroethylene (θ_{CF_2}), on an adsorbed film of octadecylamine (θ_{CH_3}) and on polyethylene (θ_{CH_2}) all decrease in the relative order $\theta_{CF_3} > \theta_{CF_2} > \theta_{CH_3} > \theta_{CH_2}$. From the values of f_{SL} it is possible to estimate that γ_S°, the free surface energy of such a film of perfluorodecanoic acid, does not exceed 25 ergs/sq. cm. The much lower surface energy is basically the reason for the recent observations[5] of a much lower coefficient of dry friction for a solid tetrafluoroethylene polymer as compared with polyethylene.

Many exceptions were found to the generalization in the literature[6] that non-polar compounds spread on non-polar solids. For example, the contact angles of carbon tetrachloride, cyclohexane and *m*-xylene on the monolayer of perfluorodecanoic acid were found to be 60, 62 and 71°, respectively.

This investigation shows that the $-CF_3$ group can be expected to occupy an interesting and unique place in surface chemistry. Compounds such as perfluorodecanoic acid are examples of a new class of amphipathic or surface-active organic compounds with $-CF_3$ groups and one or more adsorbable polar groups at opposite portions of the molecule. Such compounds possess both highly hydrophobic and organophobic properties and when close packing of $-CF_3$ groups can occur, they will have even more unusual resistance to chemical attack by bulk liquids. They may also act when adsorbed on smooth solids as excellent boundary lubricants provided the carbon skeleton of the molecule has a configuration permitting the formation of a sufficiently condensed film.

A report of the entire investigation will be made in the near future.

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PREPARATION AND PROPERTIES OF A HIGHLY ACTIVE ADRENOCORTICOTROPIC HORMONE PREPARATION[1]

Sir:

By a combination of two published methods[2,3], we have obtained a highly active adrenocorticotropic (ACTH) preparation from sheep pituitary glands. The physicochemical properties of this preparation are highly at variance with previous reports[4,5]; this warrants the present communication.

The acid–acetone extract of fresh sheep glands was fractionated with NaCl as described previously[2]; 10 g. of the NaCl precipitate was dissolved in 0.1 *M* acetic acid and adjusted to *p*H 3.5–4.0. This was followed by the oxycellulose adsorption technique of Astwood, *et al.*[3] From 1 kg. of sheep pituitaries, approximately 200 mg. of highly potent ACTH was obtained. When assayed by the adrenal ascorbic acid depletion test,[6] this product, designated as Preparation E, had a potency of 30–50 USP units per milligram. This indicates a virtually complete recovery of the hormone.

Analysis of a sample of Preparation E gave the following data: N, 16.1%, S, 0.7%, cystine, nil, tryptophan, 3%, and tyrosine, 5%. The preparation was not dialysable through cellulose casings (Visking), and had a sedimentation constant, S_{20}, of 0.8 *S*. As shown in Table I, partial pepsin and acid hydrolysis caused no loss of ascorbic acid depleting activity.

Electrophoresis on Munktell 20 filter paper was carried out in borate buffers of various *p*H and of ionic strength 0.1, at 4°, according to the technique of Kunkel and Tiselius,[7] using crystalline lysozyme as a point of reference for the migration rate of Preparation E. The paper was divided into origin,

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