findings of the Carlsberg group.[13] The following scheme is proposed

$$\begin{tikzcd} \text{Ovalbumin} \arrow[r, "B.\ subt."] & \text{Intermediate ('open') protein} \arrow[r, "B.\ subt."] \arrow[d, "\text{CXY}"] & \text{Plak. I and II + peptides} \\ & \text{Alanine + plakalbumin-like protein} & \end{tikzcd}$$

Whether the initial reaction involves the opening of a peptidic bond or only represents a configurational alteration has not been determined.

Three of the CXY preparations used in these studies were found to be contaminated with bacteria (aerobic culture on yeast extract agar). The fourth preparation, however, showed no growth although it gave similar results with ovalbumin. Still the absence of viable bacteria does not prove the absence of enzyme.

Even though the *B. subtilis* enzyme so closely mimics the action of the contaminant, the possibility that a different proteolytic enzyme, possibly of pancreatic origin, is the real contaminant must be considered.[14] In any case the importance of recognizing such possible contaminants when using CXY in studies on proteins or peptides is clear. Very low levels of contamination may, as in this case, alter the observed reaction markedly.

A more detailed report will appear in *Comptes rendus du Laboratoire Carlsberg.*

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[13] K. Linderstrom-Lang, *Lane Medical Lectures*, **6**, 73 (1952).

[14] The possibility that CXY itself is able to "open" the ovalbumin molecule and that only this function is inhibited by DFP, while not ruled out, seems unlikely.

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THE SEPARATION OF THE FOUR PLATINUM GROUP METALS PALLADIUM, RHODIUM, IRIDIUM AND PLATINUM

Sir:

The separation of the four platinum group metals palladium, rhodium, iridium and platinum has been accomplished very simply at room temperature by the use of Dowex-50 cation exchange resin. Acting on some preliminary observations on rhodium by C. I. Browne (private communication) we have found that a mixture of these elements may be separated as follows: the solution is taken near dryness repeatedly with a mixture of nitric and perchloric acids until every trace of halide ion is removed and the ions are left in a small volume (0.2–0.5 ml.) of fuming perchloric acid. The solution is then diluted to a volume of approximately ten milliliters with distilled water and is run into the top of an ion-exchange column packed with Dowex-50 resin. Under these conditions platinum will pass through the column while the other three elements adhere. The column may be washed with distilled water to remove the last traces of platinum. If any halide ions remain in the solution, the platinum fraction will contain small amounts of the other three elements.

Palladium is then stripped from the column with dilute (0.05 to 0.5 *M*) hydrochloric acid. This process occurs quite readily.

Rhodium elutes gradually from the column with 2 *M* hydrochloric acid. This process is rather slow. Experiments are in progress to determine the effect of raising the temperature of the eluting solution to increase the rate of the reactions involved.

Iridium is removed with 4 to 6 *M* hydrochloric acid. This process, like the elution of rhodium, is rather slow.

Our experiments appear to show that sulfate ion prevents the adsorption of rhodium and iridium by the resin, presumably by forming neutral or anionic complexes with the metal cations.

This separation has been used in conjunction with other simple chemical steps for the radiochemical separation of pure rhodium in good yield from uranium fission products.

Further research will be done on this process.

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RECEIVED SEPTEMBER 3, 1953

PEROXIDE-INDUCED ADDITIONS OF METHYL FORMATE TO OLEFINS

Sir:

Preliminary studies with the peroxide-induced reaction of ethyl formate with ethylene gave complex products which contained both the ethyl esters of telomeric aliphatic acids, $H-(CH_2CH_2)_x-COOC_2H_5$, and formate esters of telomeric secondary alcohols, $H-COOCH(CH_3)-(CH_2CH_2)_x-H$. Methyl formate was successfully used in the work reported here to reduce to a minimum products of the latter type, and telomeric methyl esters, $H-(CH_2CH_2)_x-COOCH_3$, have been obtained.

A solution of *t*-butyl peroxide (8.8 g., 0.061 mole) in methyl formate (600 g., 10.0 moles) was held at 130° in a glass-lined, stainless steel autoclave under a pressure of ethylene (methyl formate vapor pressure plus ethylene, 340–440 p.s.i.) until its absorption ceased (20 hours). Distillation of the reaction mixture gave unreacted methyl formate and a higher boiling product (70–80 g.). Its further distillation through a small fractionating column packed with a wire spiral gave the following products: (1) a series of fractions containing *t*-butyl alcohol and methyl propionate (5.78 g., b.p. 72–84°, n^{20}_D 1.3761–1.3827, m.p. of *p*-toluidide 123°)[1,2]; (2) methyl valerate (6.91 g., b.p. 130°, n^{20}_D 1.3980, m.p. of *p*-toluidide 69–69.5°)[2]; (3) methyl enanthate (7.94 g., b.p. 113–116° at 100 mm., n^{20}_D 1.4165, m.p. of *p*-toluidide 79.5–80°, m.p. of mixture with an authentic sample gave no depression, enanthic acid made by carbonation of *n*-hexylmagnesium bromide); (4) methyl pelargonate (6.24 g., b.p. 88–91° at 8 mm., n^{20}_D 1.4262, m.p. of *p*-toluidide 83.5°)[2]; (5) methyl hendecanoate (5.02 g.,

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[1] All toluidides were prepared by the method of C. F. Koelsch and D. Tenenbaum, THIS JOURNAL, **55**, 3049 (1933).

[2] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 222.