

Diethylstilbestrol Di-ethylmercaptoacetate.—This ester was prepared just as was the preceding ester. The purification was carried out by evaporating the ether extract to dryness and taking the residue up in 10 cc. of ether and 40 cc. of Skellysolve A. This solution was passed through activated alumina and the alumina was then extracted with 1:4 ether-Skellysolve A. The extract was evaporated and the absorption-elution process carried out twice more. Finally the crude product (1.05 g.) was crystallized once from Skellysolve B and twice

from 95% ethanol giving a yellowish product 0.30 g., m. p. 99–101°.

Anal. Calcd. for $C_{26}H_{32}O_4S_2$: C, 66.04; H, 6.83; S, 13.57. Found: C, 66.01; H, 6.73; S, 13.83.

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RECEIVED MARCH 16, 1949

COMMUNICATIONS TO THE EDITOR

THE USE OF CADMIUM IODIDE IN STARCH-IODINE COLORIMETRIC PROCEDURES

Sir:

In the course of an investigation¹ on methods of analysis for trace amounts of selenium in water, it was found that cadmium iodide and starch form a stable solution which may be used as a colorimetric reagent for a number of oxidizing substances. The reduction potential of the iodide in such a solution is a function of the pH. By proper adjustment of the pH, the iodide may be "exposed" to oxidation by oxidizing agents for controlled periods of time and in this way it was found possible to determine one oxidizing agent in the presence of others.

Cadmium iodide crystals may have a brownish discoloration which is shown by reaction with starch to be free iodine. However, after an aqueous solution of cadmium iodide is boiled for ten or fifteen minutes, a colorless solution is obtained. This solution may be added to a solution of starch to give a mixture that is apparently stable indefinitely to atmospheric oxygen and diffused sunlight.

In neutral solution, only the very strongest oxidizing agents, such as chlorine or hypochlorite, are capable of oxidizing the iodide to iodine and producing the blue starch-iodine color. At lower pH values, weaker oxidizing agents are able to oxidize the iodide; e. g., nitrous acid is capable of oxidizing the iodide if the pH is below about 4.0 but the pH must be in the neighborhood of 1.0 or lower before selenious acid is able to react. Dissolved oxygen attacks the cadmium iodide reagent only in the most highly acid solutions, and very slowly even then.

The linear starch "A-fraction" isolated by Schoch² gives the best results although commercial soluble starches can be used. The color of the A-

fraction starch-iodine complex produced by selenious acid in concentrations from 0.1 to 2.0 p. p. m., as selenium, follows Beer's law quite closely. The absorption band is broad with maximum absorption occurring at about 615 m μ .

Cadmium iodide in aqueous solution has been shown to form one or more auto-complexes, the nature of which has been the subject of several investigations. The complex anion may be CdI_3^- , CdI_4^{2-} or CdI_5^{3-} , with the cation Cd^{++} or CdI^+ .

This reagent is undergoing further investigation in connection with the development of colorimetric methods of determining traces of substances having oxidizing properties, particularly selenium as selenious acid.

We wish to thank T. J. Schoch of the Corn Products Refining Company for providing generous samples of the linear starch A-fraction.

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RECEIVED JULY 11, 1949

GERMIDINE AND GERMITRINE, TWO NEW ESTER ALKALOIDS FROM *VERATRUM VIRIDE*

Sir:

Recent evidence^{1,2} indicates that powdered roots and rhizomes of *Veratrum viride* may produce marked reductions of arterial pressure in patients with essential hypertension. We have isolated from this material two new, highly active ester alkaloids derived from the alkaline germine, which we have named germidine and germitrine.³

(1) E. D. Freis and J. R. Stanton, *Am. Heart J.*, **36**, 723 (1948).

(2) E. D. Freis, et al., *J. Clin. Investigation*, **28**, 353 (1949).

(3) Drs. E. D. Freis, J. A. Stanton and F. C. Moister of the Robert Dawson Evans Memorial, Massachusetts Memorial Hospitals, and the Department of Medicine, Boston University School of Medicine, have evaluated more than 100 of our individual alkaloidal fractions in patients with essential hypertension. Their results will be published elsewhere.

(1) This investigation is supported by a research grant from the National Institutes of Health.
(2) Schoch, *This Journal*, **64**, 2957–2961 (1942); "Advances in Carbohydrate Chemistry," Vol. I, ed. by Pigman and Wolfson, Academic Press Inc., New York, N. Y., 1945, pp. 247–277.