

## DISCUSSION

THE CHEMICAL NATURE OF "ASCORBIC ACID OXIDASE"<sup>1</sup>

As part of a general program of studies on the possible reactions of vitamin C in tissues, we have been interested in the various "enzymes" reported as occurring in plant juices that catalyze aerobic oxidation of the vitamin. If there were one or more widely distributed enzymes that served in a specific manner for the reversible oxidation of vitamin C, such evidence would have a strong bearing upon the postulated function of the vitamin in tissue respiration.

All our evidence, however, points toward a simpler interpretation of the observed phenomena and lends greater significance to the work of Barron and associates in emphasizing the rôle of copper as a catalyst for the aerobic oxidation of vitamin C. In addition to the physiological implications, the results are important in relation to methods of vitamin analysis and methods of vitamin preservation.

A detailed report will appear in another publication, but in view of the general interest of the problem for non-chemists and chemists, a brief summary of the evidence may be stated as follows:

(a) The copper content of the "enzymes" from squash and cauliflower is sufficient to account for the observed catalysis, and the greater part of the Cu in such preparations is found in the coagulated protein upon heat inactivation; (b) mixtures of copper salts with albumin exhibit properties like those of the postulated "enzymes" with respect to catalysis, inhibition, heat and acid inactivation, optimum pH and stability; (c) seven different copper inhibitors, both organic and inorganic, have the same relative effects upon pure copper compounds, copper-protein mixtures and the "enzymes"; (d) copper biuret exhibits a catalytic effect that is equivalent, atom per atom, to that of simple copper salts.

Although the above findings for plant tissue extracts suggest a possible relationship between the vitamin and copper in the living organism, there is not sufficient evidence to establish such a view-point at the present time. We do suggest, however, that there is no further need for using such terms as "ascorbic acid oxidase," "vitamin C oxidase" and "hexuronic acid oxidase" in the literature, at least in the sense that they have been used in the past.

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<sup>1</sup> Journal publication 338 from the Chemistry Department, University of Pittsburgh.

THE SELENIUM DEHYDROGENATION OF  $\alpha$ -TOCOPHEROL

EVANS, Emerson and Emerson<sup>1</sup> isolated from wheat germ oil a substance with vitamin E-like properties which they named  $\alpha$ -tocopherol. This product was a light-colored oily alcohol, showing a characteristic absorption band at 2980 Å.,  $E_{1\text{cm}}^{1\%} = 90$  ca. Analyses of both the p-nitrophenyl urethane and the allophanate indicated a provisional formula of  $C_{29}H_{50}O_2$ .

Previous observations concerning vitamin E concentrates prepared from wheat germ oil and cottonseed oil suggested that the vitamin probably belonged to either the steroids or the triterpenoid alcohols.<sup>2</sup>

In an attempt to advance the knowledge with regard to the structural nature of vitamin E, two samples of  $\alpha$ -tocopherol were subjected to dehydrogenation by means of selenium at a temperature of 300°–330°. In both experiments, the resulting mixture consisted of a volatile crystalline fraction and a fluorescent oily fraction. Purification of the volatile material by sublimation and recrystallization from dilute ethanol yielded light yellow, needle-shaped crystals having a melting point of 106°. A comparison of the physical and chemical properties of these crystals with an authentic sample of duroquinone indicated that the substance was duroquinone.

An analysis of the purified crystalline product obtained by the selenium dehydrogenation of  $\alpha$ -tocopherol was performed by Dr. Helen Stantial, of the University of Toronto, who kindly supplied the following data:

Calculated for $C_{10}H_{12}O_2$	C	73.13	H	7.37	O	19.49
Found I	C	72.76	H	7.34	O	19.90
II	C	72.97	H	7.58	O	19.45
Mean	C	72.87	H	7.46	O	19.68

It is suggested that this fraction represents a cleaved side-chain from the  $\alpha$ -tocopherol molecule and that the side-chain probably consists of two isoprene units. The fluorescent oily fraction is being investigated with a view to determining the nuclear structure of the alcohol.<sup>3</sup>

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## INFERIOR YIELDS OBTAINED FROM CROSSES OF SIX-ROWED WITH TWO-ROWED BARLEYS

OUR cultivated barleys, so far as we know, all contain 7 (haploid) chromosomes. The morphological variation is enormous. In the 6-rowed group all three

<sup>1</sup> H. M. Evans, O. H. Emerson and G. A. Emerson, *Jour. Biol. Chem.*, 113: 319, 1936.

<sup>2</sup> F. A. Askew, *Biochem. Jour.*, 29: 472, 1935.

<sup>3</sup> MS. received May 15, 1937.