

## 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.

spikelets at a node of the rachis produce one fertile flower each. In the 2-rowed group the lateral spikelets are sterile and only a single seed is produced at each node. Crosses are easily made between the two groups, and there is no evidence of sterility nor of incompatibility in their appearance. Our recent results indicate that the ease of hybridization and the complete fertility in such crosses may not tell the whole story. The 2-rowed  $\times$  6-rowed crosses are inferior in yield to either 6-rowed  $\times$  6-rowed or 2-rowed  $\times$  2-rowed. This was definitely shown in an elaborate experiment in which essentially all the 378 combinations were made between 28 parents. There were included in the test 149 crosses of 6-rowed on 2-rowed and 209 crosses of 6-rowed on 6-rowed. In 1935, 2,921 selections were made from the 378 crosses. In the years before selections were made the yields of the 6-rowed  $\times$  2-rowed crosses were decidedly lower. In 1936 the average yield of the selections from 6-rowed  $\times$  2-rowed was only 89 per cent. of that of the 6-rowed  $\times$  6-rowed crosses. This percentage would not be so striking were it not for the large numbers involved. There were 1,789 selections of 6-rowed  $\times$  6-rowed and 961 of 6-rowed  $\times$  2-rowed. Out of the 1,789, 757, or 42.3 per cent., were worthy of further trial, while only 167, or 17.5 per cent., were continued from the 961 selections from 6-rowed  $\times$  2-rowed crosses. Even this reduced number was not so promising as were those saved from the 6-rowed  $\times$  6-rowed crosses, and contained few outstanding types.

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#### THE RECRUDESCENCE OF A CONFUSING TERMINOLOGY

UNTIL the beginning of the present century all popular works on botany, and many of the text-books, failed to distinguish clearly between the sexual and non-sexual phases of plants. Indeed, there appeared from time to time discussions in which either the "homologous" or the "antithetic" nature of the alternation of generations was upheld or disapproved. Yet as early as 1851 Hofmeister had made clear that throughout all the higher groups of the plant kingdom there is a definite alternation of gametophyte and sporophyte—sexual and non-sexual generations. But people continued to speak and write of the pistil as the "female generative organ," and they spoke of the stamens as "male" organs and of "male" cottonwood trees and of "female" pine cones.

Largely through the influence of the text-book by Sydney H. Vines in England and through the teaching of Charles E. Bessey and John M. Coulter in America these ancient inaccuracies of expression dis-

appeared wholly or at least in large degree, so that the former confusion of gametophyte with sporophyte seemed a thing of the past. Practically all writings and text-books distinguished clearly the n- and 2n-generations. This happy state of affairs continued for thirty years, although it must be confessed that our horticultural and agricultural friends remained for most of the time somewhat outside the pale of morphological respectability.

But now, when the former confusion had presumably disappeared from serious botanical literature, up bobs the same old trouble in an otherwise most scholarly and excellent text-book (Wilson and Haber: *Introduction to Plant Life*, published by Henry Holt and Company, 1937). Students have difficulty enough in distinguishing the sexual from the non-sexual; when the subject is confused in their text-book an impossible situation results. It is much to be hoped that in a second edition the authors of this valuable introduction to botany will adopt a terminology in accord with present cytological knowledge and general conceptions of plant morphology.

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#### HUMAN ARTIFACTS IN ASSOCIATION WITH HORSE AND SLOTH BONES IN SOUTHERN SOUTH AMERICA

WHILE investigating the archeology of the territory along the Straits of Magellan for the American Museum of Natural History, positive evidence of the association of man with extinct horses and sloth was found in two caves. One of these caves is located in the Rio Chico Valley on estancia North Arm, just south of the Argentine-Chilean boundary; the other is about twenty miles east in Dicky Section of estancia Delgado.

In each cave the oldest cultural debris was mixed with fragments of horse and sloth bones identified by Dr. G. Simpson as *Parahipparion saldiasi* and *Mylodon listai*. Many of the bones have been burned and the long bones of the horse broken for the extraction of marrow. In one cave this oldest material had been isolated by slabs of rock and debris fallen from the cave roof. Among the artifacts associated with these bones the most noteworthy, because of subsequent changes, are the stone lance points with long flaring stems and without barbs. However, these points disappear slightly prior to the extinction of the horse and sloth and are followed by a simple bone point.

At the bottom of the layer containing the bone points are the last of the large extinct animals, after which, for a time, the people subsisted largely on birds and foxes. Among the fox bones are some identified as *Pseudalopex avus*, believed to be extinct at the present time.

In the successive layers, the following culture changes occur: above the bone points are artifacts of