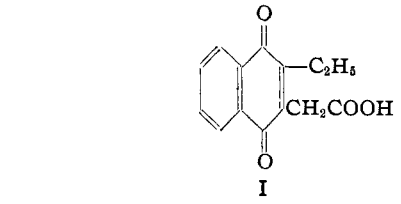
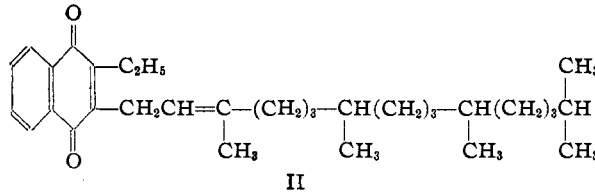
On catalytic hydrogenation vitamin K_1 absorbs four moles of hydrogen with the formation of a hydroquinone. A naphthoquinone nucleus would account for three moles of hydrogen, the fourth mole being used in the saturation of an ethylenic linkage.

Ozonolysis of the diacetate of vitamin K_1 hydroquinone resulted in the formation of a ketone which gave a semicarbazone melting at 66–67°. *Anal.* Found: C, 70.04; H, 12.13; N, 12.83, 12.88. Calcd. for $C_{19}H_{39}ON_3$: C, 70.10, H, 12.08; N, 12.91. The semicarbazone of 2,6,10-trimethylpentadecanone-14 melts at 66–67° [G. F. Fischer and K. Lowenberg, *Ann.*, **464**, 69 (1928)]. The identity of our semicarbazone with that of Fischer and Lowenberg will be tested as soon as a specimen becomes available for determination of the mixed melting point. The formation of this ketone probably indicates the presence of a phytyl side chain in the vitamin molecule.



I



II

Vitamin K_1 was oxidized with chromic acid and the oxidation products separated into neutral and acidic fractions. Two crystalline acids were obtained from the latter fractions. One of these acids crystallized from water and had a melting point of 191° in a sealed tube. It was identified as phthalic acid by conversion to the anhydride. This melted at 127–128°. When mixed with authentic phthalic anhydride (m. p. 128–129°) the melting point was 128–129°. *Anal.* Calcd. for $C_8H_4O_3$: C, 64.87; H, 2.72. Found: C, 64.78; H, 3.05.

The second solid acid which was obtained in small amounts crystallized in well-formed yellow needles and melted with decomposition at 210°. If the phytyl radical is directly united to a 1,4-quinone ring, this would presumably be a substituted naphthoquinone acetic acid. This acid, like vitamin K_1, gives no color reaction with ethyl cyanoacetate [R. Craven, *J. Chem. Soc.*, 1605 (1931)] and so is presumably substituted in both the 3 and 4 positions. *Anal.* Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.69; H, 4.85. The acid is probably 2-ethyl-1,4-naphthoquinone-3-acetic acid (I). The synthesis of this acid is at present in progress for purposes of comparison. On the basis of these degradation products we believe that the structure of the vitamin K_1 molecule is 2-ethyl-3-phytyl-1,4-naphthoquinone (II).

BIOCHEMISTRY DEPARTMENT
SCHOOL OF MEDICINE
SAINT LOUIS UNIVERSITY
SAINT LOUIS, MISSOURI
D. W. MACCORQUODALE
S. B. BINKLEY
S. A. THAYER
E. A. DOISY

RECEIVED JUNE 19, 1939

EVIDENCE FOR THE PRESENCE OF VITAMIN A AND CAROTENOIDS IN THE OLFACTORY AREA OF THE STEER

Sir:

In connection with our general project on the chemistry and sources of the fat-soluble vitamins, we became interested in examining the olfactory area of various animals for the presence of these vitamins, especially so for the presence of vitamin A's and their precursors. Since the absence of vitamin A from the diet causes the drying up of the mucous membranes of the body, it was suspected that the epithelia of the olfactory area together with the mucous membranes of the nasal passages in animals having normal diets might be rich in this vitamin. No work has been reported along these lines, and we decided to make a preliminary study of the olfactory area of the steer, but especially that area located at the upper end of the nasal cavity and known as the "yellow patch." This is composed of nerve filaments passing from the brain through the sieve-like cribriform plate into the nasal cavity and terminating at the upper third of this cavity. In the steer the epithelium of the olfactory area is dirty yellowish-brown in color while in the human being it is said to be yellow.

Forty heads of freshly killed steers were split open along the length of the nasal passages and by means of bone-cutters the olfactory area together with the bone and cartilage to which the epithelia were attached were removed. Most of the bone and cartilage were then removed from the yellowish-brown tissue, leaving a sample of about 470 g. This tissue was well ground and autolyzed with ethyl alcohol. Both the alcohol

extract and the autolyzed tissue were subjected to several extractions with pure ether in an atmosphere of nitrogen. The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate.

An absorption spectrum of the deep yellow ethereal solution in the visible spectrum showed bands at 420, 442, 478 and 655 mμ, respectively. In petroleum ether the same extract showed bands at 420, 444, 472 and 656 mμ, respectively, while the antimony trichloride color in chloroform showed prominent bands with maxima at 420, 495 and 610 mμ, respectively.

The sample was then saponified in an atmosphere of nitrogen, the non-saponifiable fraction taken up in ether, the ethereal solution filtered at 0° and an absorption spectrum taken of the filtrate in the visible region of the spectrum. It showed bands at 446 and 474 mμ, respectively. The spectrum of the antimony trichloride color showed bands at 410, 440, 495, 620 and in one case at 690 mμ, respectively. An ultraviolet absorption spectrum of this sample in ethyl alcohol is shown plotted in Fig. 1. A maximum is readily

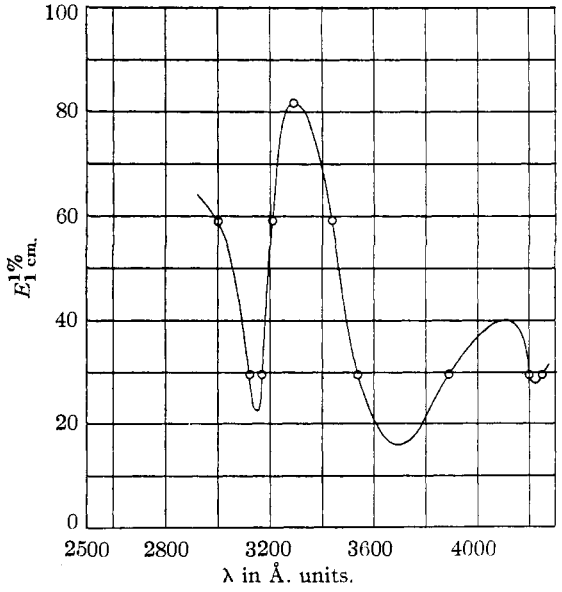


Fig. 1.

seen at 328 mμ which together with that of the antimony trichloride at 620 mμ is characteristic of vitamin A_1. The band of the antimony trichloride color at 690 mμ may be due to the presence of vitamin A_2, although the appearance of this band was not consistent. From the intensity of the maximum at 328 mμ and the concentration of the solution, we calculated $E^{1\%}_{1\ cm.}$ to be 82 for our sample which, on the basis of the purest vitamin A having a potency of 3,250,000 U. S. P. vitamin A units per gram [Milas and Heggie, unpublished results] would have a potency of 116,000 U. S. P. vitamin A units per gram. In another sample taken from a single steer head we found a potency of about 76,000 U. S. P. vitamin A units per gram.

The bands of the visible spectrum at 420, 442–446, 472–478 mμ, respectively, are due to carotenoids. We have not as yet identified the other bands reported in this paper and inasmuch as we are continuing with our work, we are hoping to report a more complete account of it later.

CONTRIBUTION NO. 193 FROM THE
RESEARCH LABORATORY OF
ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

NICHOLAS A. MILAS
WILLIAM M. POSTMAN
ROBERT HEGGIE

RECEIVED JUNE 19, 1939

THE FORMATION OF α-ETHYLTHIOGLUCOPYRANOSIDE FROM GLUCOSE ETHYLMERCAPTAL

Sir:

It has been found two years ago [Green and Pacsu, THIS JOURNAL, **59,** 1205 (1937)] that α-ethyl- and α-benzylthioglucosides [Schneider, *et al.*, *Ber.*, **49,** 2054 (1916); **51,** 220 (1918); **61,** 1244 (1928)] are furanosides and not of "normal" (pyranoid) structure as their discoverers believed. This was shown by acid hydrolysis constants, conversion into ethylglucofuranoside, and calculations from Hudson's rules of isorotation. On account of certain irregularities observed by Green and Pacsu during the process of hydrolysis, the behavior of α-ethylthioglucofuranoside in 0.01 *N* hydrochloric acid at 100° was subsequently studied [Pacsu and Wilson, THIS JOURNAL, **61,** 1450 (1939)]. It was found that in this unprecedented hydrolysis about one-half of the α-ethylthioglucofuranoside changed into glucose and mercaptan whereas the other half escaped the hydrolyzing effect of the acid by shifting the furanoid ring into the acid resistant pyranoid ring. The ring shift resulted in the formation of α-ethylthioglucopyranoside, a new thioglucoside, which was isolated and characterized by its tetraacetate. In a recent paper [Brigl, Gronemeier and Schulz, *Ber.*, **72,** 1052 (1939)] which was submitted for publication one month later but appeared one month earlier than the article of Pacsu and Wilson, Brigl and co-workers re-