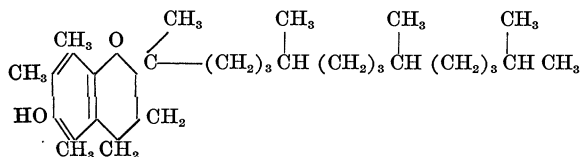


THE CHEMISTRY OF VITAMIN E. III. PERMANGANATE OXIDATION OF ALPHA TOCOPHEROL

FERNHOLZ,¹ on the basis of his degradation studies, proposed for the structure of alpha tocopherol formula I:



Formula I

By oxidizing alpha tocopherol with chromic anhydride in acetic acid solution, a lactone $C_{21}H_{40}O_2$ was obtained. The origin of such a lactone is easily explicable on the theory that alpha tocopherol contains a chromane ring; if alpha tocopherol contained a coumarane ring, a beta hydroxy acid would be expected.

Karrer and his co-workers,² by treating pseudo cumo hydroquinone with phytyl bromide, obtained a synthetic product which apparently is a mixture of alpha tocopherol and its C-2 epimer. Karrer believed that this reaction would yield a coumarane rather than a chromane, and he suggested that Fernholz's gamma lactone arose by rearrangement in acid solution. As example of this rearrangement he referred to work by Pospjehoff,³ Raichstein⁴ and Braun,⁵ where beta hydroxy acids on distillation over 20 per cent. H_2SO_4 were converted to the gamma lactones.

As further support for the chromane structure, alpha tocopherol was oxidized in acetone solution with neutral permanganate. No difficulty was experienced in isolating in good yield the $C_{21}H_{40}O_2$ lactone in the form of the benzyl thiuronium salt of its hydroxy acid. On admixture with the corresponding salt obtained by the chromic acid oxidation of alpha tocopherol, there was no depression of the melting point.

Experimental.—1.0 mg of alpha tocopheryl allophanate was saponified in the usual way. To the free tocopherol, in 50 cc of acetone, was added slowly with mechanical stirring 1.87 gm (6 moles) of potassium permanganate. The first 900 mg were rapidly decolorized; then it became necessary to warm the solution slightly. When all the permanganate had been added, the solution was refluxed until the permanganate was entirely reduced.

¹ E. Fernholz, *Jour. Am. Chem. Soc.*, 60: 700, 1938.

² P. Karrer, H. Fritsche, B. H. Ringier and N. H. Salomon, *Helv. Chim. Acta*, 21: 520, 1938.

³ Pospjehoff, *Jour. Russ. Phys. Chem. Soc.*, 29: 372, 1897.

⁴ Raichstein, *Jour. Russ. Phys. Chem. Soc.*, 39: 587, 1907.

⁵ Braun, *Monatshefte f. Chemie*, 17: 210, 1896.

The solution was cooled, diluted with water, and the manganese dioxide reduced with SO_2 . A few drops of HCl were added to make the solution acid to Congo red, and the reaction mixture was extracted with ether. The ether was washed with water and then dilute NaOH to remove free acids. The total neutral fraction weighed 428 mg. This was refluxed with 15 cc of 4 per cent. methyl alcoholic KOH for one hour, then diluted with water and extracted with ether. The ether residue amounted to 238 mg, most of which could not readily be distilled in a molecular still.

The dilute alcoholic KOH solution was acidified, and extracted with ether, giving 155 mg of the lactone fraction. This was distilled in a molecular still at 120 degrees, yielding 117 mg of purified lactone. This was converted to the benzyl thiuronium salt, giving 105 mg of the salt melting at 116 to 118 degrees which gave no depression on admixture with the corresponding salt obtained from the chromic anhydride oxidation of alpha tocopherol.

Analysis: Calculated for $C_{29}H_{52}N_2SO_3$: C 68.45; H 10.30; N 5.50. Found: C 68.77, 68.56; H 10.27, 10.10; N 5.67, 5.61.

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