structure be called 8(14),9-steradiene-6,7,11,12-tetracarboxylic-6,7,11; 12-dianhydride.

BUREAU OF ANIMAL INDUSTRY
UNITED STATES DEPARTMENT OF AGRICULTURE
BELTSVILLE, MARYLAND
LEWIS W. BUTZ
ADAM M. GADDIS
ELEANORE W. J. BUTZ
RUSSELL E. DAVIS

RECEIVED MARCH 18, 1940

FURTHER COMPOUNDS HAVING ANTI-HEMORRHAGIC ACTIVITY

Sir:

In an investigation involving the synthesis and assay of a number of additional naphthoquinones and derived or related products, considerable data have been accumulated on the problem of correlating vitamin K activity and structure which will be presented after completion of adequate assays on the entire series of compounds synthesized in the two Laboratories. In the meantime we wish to report certain observations from the synthetic work and give some indication of the potencies of the new compounds.

The method developed by one of us for the synthesis of vitamin K_1 [Fieser, THIS JOURNAL, **61**, 2559, 3467 (1939)] has been found capable of wide application. By using 1,4-naphthohydroquinone as one component 2-geranyl, 2-farnesyl, and 2-phytyl-1,4-naphthoquinone have been synthesized in good yield. The phytyl compound [yellow oil, found: C, 82.82; H, 10.31] is the most active member of the series and gives a full response in the chick assay at 50 γ. Similarly the 3-farnesyl derivative of 2-methyl-1,4-naphthoquinone [found: C, 82.97; H, 8.98] is more potent than the 2-geranyl derivative but somewhat less active than vitamin K_1. The synthesis is also applicable in the benzohydroquinone series. 2,3,5-Trimethyl-6-phytyl-1,4-benzoquinone [yellow oil, found: C, 81.04; H, 11.00, hydroquinone diacetate, m. p. 56°] shows no vitamin K activity but it provides a new route to a vitamin E factor. By treatment with stannous chloride in acetic-hydrochloric acid the quinone was converted smoothly into α-tocopherol, identified through the allophanate, m. p. 175–176°, and *p*-nitrophenylurethan, m. p. 130°. Butadiene-toluquinone condenses with phytol under the usual conditions but at the reflux temperature, giving rise to 2 - methyl - 3 - phytyl - 5,8 - dihydro - 1,4 - naphthoquinone [found: C, 82.27; H, 10.86], which is active at a level of 5–6 γ. By hydrogenating synthetic vitamin K_1 and purifying the products in the form of the solid hydroquinones, the β,γ-dihydride (active at 6 γ, hydroquinone diacetate, m. p. 57–58°) and β,γ,5,6,7,8-hexahydride (slight activity, diacetate derivative, m. p. 53°) have been obtained in analytically pure form. Both butadiene-toluquinone and 2-methyl-5,8-dihydro-1,4-naphthohydroquinone show marked activity, the latter at dosages as low as 8 γ.

A by-product of the vitamin K_1 synthesis, characterized as a ketonic substance of the formula $C_{31}H_{48}O_2$ [found: C, 82.38; H, 10.65; maxima at 253 and 300 mμ; 2,4-dinitrophenylhydrazone m. p. 107–108°], shows moderate vitamin K activity (50 γ). The Zerewitinoff determination indicates the presence of one active hydrogen and one carbonyl group. Aluminum isopropylate reduction gives a diol, probably $C_{31}H_{52}O_2$ [found: C, 81.52; H, 11.48], and pyrolysis of the by-product gives rise to small amounts of vitamin K_1. The isomeric naphthotocopherol [found: C, 82.30; H, 10.69; maxima at 246 and 320 mμ; *p*-nitrobenzoate, m. p. 84–85°] is active at a higher level (300 γ); on oxidation it yields a yellow hydroxyquinone [found: C, 79.19; H, 10.17].

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY, CAMBRIDGE, MASS. L. F. FIESER
RESEARCH LABORATORIES, MERCK AND CO., INC., AND MERCK INSTITUTE FOR THERAPEUTIC RESEARCH
RAHWAY, NEW JERSEY
M. TISHLER
W. L. SAMPSON

RECEIVED MARCH 20, 1940

THERMAL DECOMPOSITION OF ACETONE CATALYZED BY IODINE

Sir:

Several investigators[1] have shown that small amounts of iodine sensitize the thermal decomposition of various organic compounds. In the case of acetone, Bairstow and Hinshelwood[1a] have reported that the decomposition was not appreciably affected by the presence of iodine. However, Rice and Weiler[2] observed that the decomposition of acetone containing methyl iodide was appreciably faster than the rate for pure acetone. Moreover it was found that the addition of approximately 1% of ethyl iodide enormously increased the rate of decomposition of acetone at 526°.[3] When a small amount of ethyl iodide was allowed to decompose completely in the reaction vessel first and then the acetone added, a large increase in the rate also was observed. This

[1] (a) Bairstow and Hinshelwood, *J. Chem. Soc.*, 1147 (1933); (b) P. A. K. Clusius, *ibid.*, 2607 (1930); (c) Faull and Rollefson, THIS JOURNAL, **58**, 1755 (1936); Rollefson and Garrison, *ibid.*, **62**, 588 (1940).

[2] Weiler, Dissertation, Johns Hopkins University, 1930.

[3] Rice and Walters, unpublished results.