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 COMMUNICATIONS TO THE EDITOR
 

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THE ISOLATION OF VITAMINS K<sub>1</sub> AND K<sub>2</sub>

Sir:

Although for some months we have been in possession of two pure substances possessing vitamin K activity, our failure to obtain crystalline derivatives has deterred us previously from reporting our data. Evidence that the crystalline compound obtained from putrefied fish meal [*Proc. Soc. Exptl. Biol. Med.*, **40**, 482 (1939)] is actually a vitamin and not an inactive compound upon which the vitamin is adsorbed is based on (a) recovery of crystals with unchanged melting point and potency after partial destruction by passage through a column of alumina, by partial oxidation with potassium permanganate or by partial destruction during distillation, (b) the similarity of the ultraviolet absorption spectra, lability toward light and chemical properties between the compounds isolated from alfalfa and from putrefied fish meal, (c) twenty recrystallizations of the fish meal compound from a variety of solvents without loss of potency, and (d) the preparation of several different batches of this compound having the same melting point and potency. Having finished the points just cited we were preparing our data for publication when we saw a report describing the preparation of a highly purified oil with vitamin K activity [*Helv. Chim. Acta*, **22**, 310 (1939)]. For their best preparation Dam, *et al.*, obtained an extinction coefficient of  $E_{1\text{ cm.}}^{1\%} = 280$  at 248 m $\mu$ . Since our compound from alfalfa gives an extinction coefficient of 385 the purity of Dam's active oil may be approximately 70%.

At room temperature vitamin K<sub>1</sub> from alfalfa is a light yellow oil which changes into a beautifully crystalline condition upon adequate cooling of an acetone or alcohol solution. Several preparations of this compound have been obtained; all have a potency of about 100 units per mg. [*Proc. Soc. Exptl. Biol. Med.*, **40**, 478 (1939)]. Vitamin K<sub>2</sub> from putrefied sardine meal is a light yellow crystalline solid with a melting point of 50.5–52°. Various preparations of this crystalline compound have uniformly shown a potency of approximately 600 units per mg. Neither compound shows optical activity with sodium

light in a 1% solution in absolute alcohol. Nitrogen, sulfur, phosphorus, and halogens are absent. Analyses of K<sub>1</sub> gave: C, 82.76, 82.54; H, 10.65, 10.66; mol. wt. (Rast), 443, 464. Calcd. for C<sub>32</sub>H<sub>48</sub>O<sub>2</sub>: C, 82.70; H, 10.41; mol. wt., 464; for C<sub>32</sub>H<sub>50</sub>O<sub>2</sub>: C 82.33; H, 10.80; mol. wt., 466. Analyses of K<sub>2</sub> gave: C, 84.43, 84.57; H, 9.87, 9.73; mol. wt., 552, 561. Calcd. for C<sub>40</sub>H<sub>54</sub>O<sub>2</sub>: C, 84.74; H, 9.61; mol. wt., 566; for C<sub>40</sub>H<sub>56</sub>O<sub>2</sub>: C, 84.44; H, 9.93; mol. wt., 568. K<sub>1</sub> shows maxima at 243, 248, 261, 270, and 323 m $\mu$ ; K<sub>2</sub> at 249, 261, 269, and 320. Radical changes in the absorption curves and loss of potency are produced by exposure to light.

Upon hydrogenation K<sub>1</sub> absorbed eight atoms and K<sub>2</sub> eighteen atoms of hydrogen. In each case a colorless product was formed which on exposure to air was oxidized to a yellow product similar to the original vitamin in color. These yellow oxidation products absorb one mole of hydrogen to form the colorless compounds again. This behavior, the absorption spectra and lability toward light and alkali, indicate a quinoid structure for these vitamins.

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 HALOGENATION OF OPTICALLY ACTIVE TERTIARY CARBINOLS

Sir:

Much work has been done on the halogenation of optically active secondary carbinols in connection with a study of the Walden inversion, but almost none has been done with optically active aliphatic tertiary carbinols. In view of the recent work of Levene and Rothen<sup>1</sup> on secondary carbinols, we wish to report the result of two years of work with an optically active tertiary carbinol.

We find that optically active tertiary carbinols of the simple aliphatic type can be converted into optically active halides by various halogenating reagents under very mild conditions, and that

(1) Levene and Rothen, *J. Biol. Chem.*, **127**, 237 (1939).