
COMMUNICATIONS TO THE EDITOR

THE ISOLATION OF VITAMINS K₁ AND K₂

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 μ . 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 K₁ 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 K₂ 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 K₁ gave: C, 82.76, 82.54; H, 10.65, 10.66; mol. wt. (Rast), 443, 464. Calcd. for C₃₂H₄₈O₂: C, 82.70; H, 10.41; mol. wt., 464; for C₃₂H₅₀O₂: C 82.33; H, 10.80; mol. wt., 466. Analyses of K₂ gave: C, 84.43, 84.57; H, 9.87, 9.73; mol. wt., 552, 561. Calcd. for C₄₀H₅₄O₂: C, 84.74; H, 9.61; mol. wt., 566; for C₄₀H₅₆O₂: C, 84.44; H, 9.93; mol. wt., 568. K₁ shows maxima at 243, 248, 261, 270, and 323 m μ ; K₂ at 249, 261, 269, and 320. Radical changes in the absorption curves and loss of potency are produced by exposure to light.

Upon hydrogenation K₁ absorbed eight atoms and K₂ 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 Rothen¹ 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).

with hydrogen chloride we can obtain either enantiomeric halide (to be sure partially racemized²) depending on the temperature of the reaction. Thus with hydrogen chloride in pentane solution at 25°, 3,7-dimethyloctanol-3, b. p. 89.0° (15 mm.), n_D^{25} 1.4320, d_4^{25} 0.8250, α_D^{25} -0.45°, yielded the corresponding tertiary chloride, b. p. 71.0° (9 mm.), n_D^{25} 1.4346, d_4^{25} 0.8647, α_D^{25} -0.28°. The same reaction run at -78° gave the enantiomeric chloride (contaminated with unchanged carbinol), b. p. 69-70° (8 mm.), n_D^{25} 1.4340, d_4^{25} 0.8516, α_D^{25} +0.17°.

These results undoubtedly are due to a predominance of one type of substitution reaction over the other, and are in harmony with the results of Levene and Rothen with phenylated carbinols, except that these investigators observed similar results only when no solvent was used. It appears then that tertiary carbinols

(2) It is not possible at present to say whether this racemization is due mainly to the concurrent formation of both enantiomers by different paths, to racemization of a sterically unstable intermediate, or to racemization due to a common ion effect.

react in much the same way as secondary carbinols, *i. e.*, that halogenation may occur by at least two different paths,³ predominance of each being determined by the temperature. If the lower temperature favors retention of the original configuration, as suggested by Levene and Rothen, thus probably involving an intramolecular nucleophilic change (S_Ni),⁴ then levo 3,7-dimethyloctanol-3 is configurationally related to dextro 3-chloro-3,7-dimethyloctane. This relationship would mean that this tertiary carbinol is an exception to the general rule advanced by Cowdrey, Hughes, Ingold, Masterman and Scott for secondary carbinols.⁵ A detailed report of our work, together with more recent developments, will be presented in the near future.

(3) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937).

(4) Ref. 3, p. 1269.

(5) Ref. 3, p. 1268.

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NEW BOOKS

Principles of Flotation. By IAN W. WARK, Ph.D., D.Sc., Officer in Charge of the Flotation Research Laboratory in the Department of Chemistry, University of Melbourne. Australasian Institute of Mining and Metallurgy, Inc. Tait Book Company Pty., Ltd., 349 Collins Street, Melbourne, Australia; G. E. Stechert and Company, 31 East 10th Street, New York, N. Y., 1938. 346 pp. 101 figs. 15.5 × 24 cm. Price, 21s./-.

This very readable, well-written monograph critically examines and correlates the more recent investigations in the field of mineral flotation with the author's numerous contributions to this important division of applied surface chemistry. In the integration of his own work with that of other investigators he has, in some instances, used their data in drawing interesting and thought-provoking conclusions.

In the presentation of the work of some investigators on homologous series of flotation reagents, Wark has neglected to recalculate and replot their data to the mole per ton basis; he has kept the pound per ton basis given in the original reports. The pound per ton basis may be important in cost studies of homologous series of flotation reagents, but such a basis does not readily permit a sound interpretation of such physico-chemical data.

In his discussion of the theory of froth formation, Wark

tells us that most inorganic salts raise the surface tension of water. However, the work of Jones and Ray and the more recent theoretical considerations of Langmuir show that, in extremely dilute solutions, all of these salts may be expected to reduce the surface tension of water.

In applying the Gibbs adsorption theorem to frothing agents, Wark remains content with the statement that since the slopes of the surface tension-concentration curves of all such reagents are negative, U is positive, and that the distorted surface of a bubble will have a lower reagent concentration and hence a higher surface tension. The evident possibility of classifying the effectiveness of such reagents according to the degree of negativity of the slopes of their surface tension-concentration curves has not been considered. Wark does show, however, that the surface tension changes due to the presence of frothing agents have a negligible effect on contact angles.

Wark has compared and discarded former erroneous ideas and theories of many investigators; he invites criticism of his interpretations. He has presented his considered opinion of the fundamentals of mineral flotation based on his own researches and those of others. The book is a valuable contribution to the science of mineral flotation.

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