COMMUNICATIONS TO THE EDITOR

THE SPECTROPHOTOMETRIC ANALYSIS OF FATS

Sir:

In view of the increasing interest in the use of absorption spectrophotometry in the quantitative analysis of glyceride fats and oils, we should like to record further useful data in regard to spectrophotometric standards.

We have found the method of Mitchell, Kraybill and Zscheile[1] extremely useful in the examination of many fats and oils, since it allows positive identification of polyene systems occurring in small amounts. In the examination of animal fats, however, in which small amounts of arachidonic acid occur, it is not possible to make quantitative analysis for the arachidonic acid without a reference standard.

We have, therefore, subjected purified methyl arachidonate exactly to the same procedure of alkali isomerization as was described,[1] and calculated the absorption coefficients at or near the principal maxima.

The sample of methyl arachidonate was obtained through the courtesy of J. B. Brown, Ohio State University, and was believed to have a purity of 95%. To date, samples of higher purity have not been obtained by us, although it is our aim to prepare samples of greater purity.

The data were obtained with a Beckman model DU photoelectric spectrophotometer,[2] using ethanol as the solvent. The maxima at 2375 and 2690 Å. have wave lengths slightly different from those for the corresponding maxima for isomerized linoleic and linolenic soaps (2340 and 2680 Å.). Therefore, the analytical constants for the arachidonic acid were obtained at exactly 2340 and 2680 Å. so that these values will fit into the scheme for analysis of mixtures of the three acids. The principal maxima characteristic of the conjugated tetraene system were observed at 3010 and 3160 Å. The specific absorption coefficients at the wave lengths used for analytical purposes were obtained as the result of four independent isomerizations. They were calculated by the use of the Lambert–Beer equation,[1] assuming 95% purity of the methyl arachidonate and converting the observed absorption values to 100% purity on the free acid basis.

While we recognize the desirability of confirming these values or modifying them, if necessary, through the use of samples of 100% purity prepared by various procedures, we feel that these constants should be made public at this time as a means of extending the usefulness of absorption spectrophotometry in the study of fats and oils.

Specific absorption coefficients at the wave lengths important for analytical purposes are listed below. The values obtained on highly purified linolenic and linoleic acids are included, as obtained by the use of the Beckman instrument.

TABLE I

REFERENCE VALUES FOR USE IN SPECTROPHOTOMETRIC ANALYSIS

Isomerized fatty acid soap	Specific absorption coefficients, Å. at— 2340	2680	3010	3160
Arachidonic	59.3	53.4	25.8	22.6
Linolenic	60.9	53.2	..	..
Linoleic	86.0	..	..	..

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[1] Mitchell, Kraybill and Zscheile, *Ind. Eng. Chem., Anal. Ed.*, **15**, 1 (1943).

[2] Cary and Beckman, *J. Opt. Soc. Am.*, **31**, 682 (1941).

ADSORPTION OF FATTY ACID BY THE LINEAR COMPONENT OF CORN STARCH

Sir:

Recent investigations in this Laboratory indicate that the adsorption of iodine by corn starch is markedly repressed by the presence of fatty acid. Thus, commercial corn starch (containing 0.65% natural fatty material) will adsorb 4.1–4.4% iodine, as determined by a modification of the potentiometric procedure of Bates, French and Rundle.[1,2] Removal of the contained fatty acid by Soxhlet extraction with 81% aqueous dioxane raises the iodine affinity to 5.3%.

It appears that this effect is due to preferential adsorption of fatty acid by the presumed linear-chain component of the starch, *viz.*, that component which is selectively precipitated by butanol[3] and which is responsible for the blue adsorption complex with iodine. Thus a sample of recrystallized butanol-precipitated fraction from corn starch adsorbed 18.7% iodine; addition of 2, 5 and 10% palmitic acid (calculated on the basis of the dry fraction) reduced the iodine affinity to 12.4, 3.5 and 0%, respectively.

The higher fatty acids likewise act as selective precipitants for the linear-chain component of corn starch. Three liters of a 2% defatted corn starch paste was autoclaved to disintegrate granule structure, then treated with 200 ml. of oleic acid and slowly cooled to room temperature with continuous stirring. The linear-chain fraction separated as a microcrystalline floc which was removed by supercentrifuging, in amount equiva-

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[1] F. L. Bates, D. French and R. E. Rundle, THIS JOURNAL, **65**, 142 (1943).

[2] E. J. Wilson, Jr., T. J. Schoch and C. S. Hudson, *ibid.*, **65**, 1380 (1943).

[3] T. J. Schoch, *ibid.*, **64**, 2957 (1942).

lent to 29% of the original defatted corn starch. After prolonged Soxhlet extraction with methanol, its iodine affinity was 14.5%. The nonprecipitated fraction (presumably of branched molecular configuration) was isolated by treating the centrifugate with several volumes of methanol. After extraction with methanol, its iodine affinity was less than 0.2%.

Since traces of higher fatty acid will prevent the adsorption of iodine, cereal starches must be exhaustively defatted before potentiometric evaluation of iodine affinity. The proportion of linear-chain component in corn starch can be approximated by dividing the iodine affinity of defatted corn starch (*viz.*, 5.3%) by that of the repeatedly recrystallized butanol-precipitated fraction (*viz.*, 19.0%). This gives a calculated amount of 28% linear-chain component in corn starch, substantially higher than the amount previously reported by selective precipitation with butanol, but in excellent agreement with values more recently obtained by improved precipitation methods with certain of the amyl alcohols. These new procedures will be reported in the near future.

Taylor and his co-workers[4] presumed the so-called α-amylose of corn starch to be the fatty acid ester of a carbohydrate. It is now apparent that this material was part of the linear-chain starch fraction, rendered polar through adsorption of natural fatty acids in the corn starch and hence migrating in the electrophoretic cell. On the basis of present information, it is presumed that the natural fatty acids in corn starch are adsorbed on the linear-chain component.

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[4] T. C. Taylor and J. M. Nelson, *ibid.*, **42**, 1726 (1920); T. C. Taylor and H. A. Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

NEW BOOKS

The Science of Explosives. An Introduction to their Chemistry, Production, and Analysis. By MARTIN MEYER, Professor and Chairman of the Department of Chemistry, Brooklyn College, and Consulting Chemist. Thomas Y. Crowell Company, 432 Fourth Avenue, New York, N. Y., 1943. xi + 452 pp. 74 figs. 14.4 × 22 cm. Price, $4.50.

The purpose of this book is to assemble, in one volume, material in the field of explosives "written in a relatively simple and readable style." It is the intent of the author "to emphasize a fundamental and practical viewpoint and to avoid the tendency to make it a text book of synthetic organic chemistry." The scope of the book can be judged by the chapter headings: 1, A General Survey; 2, The Nature of Explosives; 3, Black Powder, Pyrotechnics and Incendiaries; 4, Nitrocellulose and other Nitropolysaccharides; 5, Nitroglycerine and Related Explosives; 6, Elementary Theory of Explosive Action; 7, Grain Size and Shape; 8, The Problem of Nitration; 9, Sulphuric Acid; 10, Nitric Acid, the Fixation of Nitrogen, and Ammonium Nitrate as an Explosive; 11, Smokeless Powder; 12, T.N.T. Nitro Compounds in General and Other Explosives, Including Gases; 13, Chemistry of Initiators; Explosion Flame; 14, Practical Explosive Devices; 15, Practical Initiating Devices; 16, Inspection and Analysis; 17, Application and Use; 18, Packing, Shipping, Storage and Safety.

From the above list, it is obvious that the author has succeeded in his attempt to avoid emphasis on the synthetic aspect of explosives chemistry. The information which is given on methods of manufacture and on specification tests has been taken from the War Department Technical Manual on "Military Explosives" (TM 9-2900) and may, therefore, be considered as authoritative.

The author's objective of simplicity in style has not always been achieved. For example, "An explosive is probably most easily defined, with substantially equal accuracy, as a material which under some circumstances will behave explosively as just stated, as in any other way." Also, "T.N.T. . . . crystallizes excellently well . . .," and "For military purposes, T.N.T. can be used for all types of bursting charges, including armor piercing, although it is slightly too sensitive for that purpose and has been replaced by ammonium picrate."

It is difficult to decide what previous training is expected of people who use this book. The statement is made "sulphuric acid has the formula H_2SO_4," and the use of the chemical balance is described in detail. On the other hand, ammonium nitrate is reported to present five polymorphic forms, and no explanation is given of the meaning or significance of this statement. It would also seem likely that any student able to follow the calculation of the muzzle velocity of a projectile, as given in Chapter 6, would have had some technical training.

Many people in the field of explosives will object to the accuracy of the information presented. The statement that "an outstanding feature of the otherwise colossal American war program is the apparent underestimate of explosive requirements" cannot be excused by the qualification "as indicated by the published figures." It should certainly be realized that published figures might not indicate the total production, and this criticism is an injustice of the Ordnance Department. The truth is that production of explosives has been one bright spot in the war and that at no time have the armed forces had to consider an insufficient supply of explosives in planning their operations. Exception may also be taken to the statement "nothing like the necessary quantity of nitric acid is anywhere in sight in the United States." There will be many who will not agree that TNT should be classified as a detonator, that sensitivity increases with the number of nitro or nitrate groups, that brisant explosives are those with a detonation rate of over 1000 meters per second, or that bomb tests are performed in the field and the chemist has little to do with them. Some organic chemists will not approve of the statements that the nitration of hydrocarbons is a reversible reaction and "nitric acid is characterized by the reaction with organic materials which makes it useful for explosive work and it acquires this property at lower concentrations as the case of nitration increases."

The author has not treated very new developments at length because they "are readily understood by one versed in fundamentals" and because they "will later, prove to be much less startling than their present build-up makes them