

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 Zscheile¹ 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.

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

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

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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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 butanol³ 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-

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

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

(3) T. J. Schoch, *ibid.*, **64**, 2057 (1942).