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Report on

SPECTROPHOTOMETRIC DETERMINATION OF PERCENT CONJUGATION OF DRYING OILS

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ABSTRACT

This report deals with a relatively new method of determination of the percent conjugation in drying oils. The results of this method are comparably reported with the results of the Ellis-Jones (modified) Diene Method which was previously used in these studies. Conclusions and recommendations are made regarding the future use of this method in specifications for drying oils to be used in protective coatings.

INTRODUCTION

A. Authorization

1. These studies were authorized by Bureau of Aeronautics letter of 20 April 1942, Aer-E-2574-MVD F38(6-7), NP14, F38-2(12).

B. Statement of Problem

2. Many difficulties have been experienced in the analysis of drying oils and their related products. In the work on a substitute for tung oil, to be used in Navy specification protective coatings, it was found advisable to utilize a quick but accurate method of determining the percent conjugation in the proposed substitutes. This more rapid method is desirable not only because of the large number of samples studied but because the current method yields rather inconsistant results, necessitating additional work.

C. Known Facts Bearing on the Problem

3. A short review of the drying process of oils may afford a better understanding of the mechanism of this method. Oils dry by one or both of two means (1) oxidation and (2) polymerization. Both of these depend upon unsaturation in the oil molecule. The speed with which the drying takes place is also dependent upon the degree of conjugation of the double bonds. As an example, linolenic acid (9, 12, 15 Octadecatrienoic acid) would have a much slower drying time when incorporated in the oil as a glyceride than would pseudoeleostearic acid (10, 12, 14 Octadecatrienoic acid). Triply conjugated systems have a greater affinity for oxidation and polymerization than do doubly conjugated systems. This is exemplified by the fact that tung oil, which is composed for the most part of the glycerides of eleostearic acid (9, 11, 13 Octadecatrienoic acid), has a much faster drying time than linseed oil, the glycerides of which are mostly of linoleic acid (9, 12 Octadecadienoic acid). From this discussion it also follows that conjugated linoleic (9, 11) would be faster drying as the oil glycerides than would linoleic (9, 12). It is therefore of prime importance to know the percent of conjugation in an oil in order to better understand and predict its behavior.

4. In the last several years use of the spectrophotometer has been reported to give reliable results. It has been known for some time that doubly and triply conjugated double bonds will absorb light in the ultraviolet region of the spectrum. Various investigators have now found that doubly and triply conjugated double bonds have maximum absorptions at certain specific wave lengths. This absorption also has been found to follow Beer's Law, which states that the extinction is a linear function of the concentration, and Lambert's Law, which states that extinction is a linear function of the thickness of solution or solids; hence, these laws combined may be expressed as:

$$E = \text{Log} \frac{I_o}{I} = kcd \qquad \text{where:}$$

E = extinction or logarithm of the ratio incident light to transmitted light,

I_o = intensity of the incident beam,

I = intensity transmitted by the material,

k = the specific extinction for a unit concentration and unit thickness and, therefore, a constant, independent of concentration or thickness,

c = concentration of material added,

d = thickness through which the light must travel.

This formula has been used as the basis of practically all calculations in spectrophotometry and a modification of it will be used in this report.

METHOD

A. Apparatus

5. The Beckman Quartz Spectrophotometer, Model DU, with the ultraviolet attachment (Plate 1) was used in making these measurements. Quartz transmission cells which were supplied by the manufacturer as having been matched to ±0.005 cm. from window to window and 10 cm. in height were used to contain the sample and blank. Specially purified acetone was used as the washing solvent and specially purified cyclohexane and ethanol were used as dilution agents. The acetone and cyclohexane were purified by distillation and subsequent perculation through Silica Gel, manufactured by the Davison Chemical Corp. The assembly for the perculation is shown in Plate 2.

B. Materials

6. Ethanol, as well as the previously mentioned acetone and cyclohexane, was purified of aldehydes by the silver oxide precipitation method and after standing for 24 hours was distilled. All solvents, etc. were stored in oil-free, glass-stoppered Pyrex bottles. Several commercial oils were also used in these studies. These are given in Table I.

TABLE I

COMMERCIAL OILS USED IN THESE DETERMINATIONS

	Material	Manufacturer
1.	Tung Oil	Received from Norfolk Navy Yard
2.	Linseed Oil	Spencer-Kellogg Co.
3.	Baker's Special Dehydrated Castor Oil	Baker Castor Oil Co.
4.	Castung No. 103	Baker Castor Oil Co.
5.	Castung No. 403	Baker Castor Oil Co.
6.	Roosenol 100	H. D. Roosen Co.
7.	Roosenol 200	H. D. Roosen Co.
8.	Dehydrol	Sherwin-Williams Co.
9.	Isoline Fatty Acids	Worburn Degreasing Co.
10.	Isomerized Castung Special Fatty Acids	Prepared at NRL from Baker's Castung Special
11.	Isomerized Linseed Fatty Acids	Prepared at NRL from Linseed Oil

C. Experimental

(1) Spectrophotometric Ultra-Violet Absorption

7. Approximately a 0.2 gram sample of oil or acids was weighed accurately into a 50 ml volumetric flask and made up to volume with purified cyclohexane. A 1 ml aliquot was diluted to volume with purified ethanol in a 100 ml volumetric flask. These are empirical concentrations; the optimum concentration is varied according to the percent conjugation of the sample. This is usually derived by experiment. The concentration should be adjusted so that the percent transmission remains within the range of 85% to 25%. A blank was prepared, using the same concentration of solvents, placed in one of the matched cells, and the instrument was adjusted to 100% transmission. The transmission of the sample was read in relation to this. The value was converted to unit concentration by the formula:

$$\text{Specific Alpha} = \frac{\text{Log}_{10}\ \frac{a}{b}}{cl}$$ where:

Specific Alpha = specific absorption coefficient or alpha,
a = incident light (100%)
b = percent transmission of the sample,
c = concentration in grams per liter,
l = the thickness, in centimeters, of the solution.

It is necessary to exclude all traces of aromatic solvents from these samples before making these solutions since aromatics also have high absorptive powers for ultra-violet light.

(2) Ellis-Jones Method (Slight Revision)(Ref. 1).

8. About 2.0 gms of the oil was accurately weighed into a 200 ml round-bottomed flask, fitted with a standard-taper, ground-glass joint. Twenty-five ml of a 10% solution of maleic anhydride in xylene was added, an air-cooled reflux condenser was attached, and the flask was heated to reflux (145° to 160°C.) for three hours. The contents were then cooled; approximately 15 ml of distilled water were added through the condenser and refluxing (100° to 120°C.) was continued for 15 minutes; then the sample was cooled to room temperature. Ether and distilled water were washed through the condenser and the contents of the flask were transferred to a 250 ml separatory funnel, followed by three rinses with 8 ml portions of ether and then by three 5 ml portions of distilled water. The contents were shaken well and the layers were allowed to separate. The aqueous layer was drawn off into a 250 ml Erlenmeyer flask, the xylene was extracted twice with 20-25 ml portions of distilled water and this extract also added to the original aqueous layer. The combined aqueous extracts were titrated with 0.5N sodium hydroxide using phenolphthalein indicator. A blank of 25 ml of maleic anhydride reagent was carried through the procedure simultaneously. The difference in the NaOH titer between blank and sample was calculated as the amount of maleic anhydride combined with the oil. The percent conjugation was calculated as:

$$\frac{(\text{Blank} - \text{Titration of Sample}) \times \text{Normality} \times 146.67}{\text{Wt. of Sample}}$$

(3) Isomerization of Oil.

9. 300 gms of linseed or castor oil were heated in a large beaker with 100 gms of potassium hydroxide and 600 gms of glycerine. The mixture was heated to 185°C. in one-half hour at which time a sample of 100 ml was taken. Other samples were taken at half-hour intervals until seven samples had been obtained. The samples were immediately acidified with twice the theoretical amount of sulfuric acid, the mixture of precipitated fatty acids and solution was heated, and carbon dioxide gas was bubbled through.

Each sample was washed with distilled water in this manner until the wash was free of acid. The samples were then stored in a closed vial under carbon dioxide after being dried with anhydrous sodium sulfate.

DISCUSSION OF RESULTS

10. Upon a survey of the literature, the following values in Table II were found for percent conjugation of tung and dehydrated castor oils as well as linseed and castor oils.

TABLE II

ANALYSIS OF SOME TYPICAL RAW OILS BASED ON PERCENT TOTAL ACIDS

Oil	% 2-Bond of Total Acids	% 3-Bond of Total Acids	% 4-Bond of Total Acids	Reference
1. Tung	0.0	84.5	0.38	Ref. 2
2. Dehydrated Castor	28.4	0.19	0.0	
3. Linseed	0.69	0.12	0.04	
4. Castor	0.23	0.24	0.0025	
5. Tung		76-82		Ref. 3
6. Tung		74.5-76.7		Ref. 4
7. Tung		86.3		Ref. 5
8. Tung		86.0		Ref. 6

11. It is obvious from examination of Table II that consistant results have not been reported on the percent conjugation of the various oils. Some data, not given in Table II, varied more than 10%. Conclusions may be drawn that these variations can be attributed to either inconsistant composition of the oils or the method by which the results were derived. Since spectroscopic assays of oils have only been utilized in the last three to five years, the values reported by Bradley and Richardson (Ref. 2) and their references have been used for comparison.

12. In order to establish a concentration curve for percent triene conjugation, various data were obtained from the literature for comparative purposes. Kaufmann, Baltes and Funke (Ref. 7) and Miller and Kaas (Ref. 8) reported K3700 (270 mu) as 189 for the specific absorption coefficient for 100% alpha eleostearic acid. On the other hand, Bradley and Richardson (Ref. 2) reported a value of 168 at this wave length. Due to difficulties of isolation of the alpha acid, an indirect approach was made to ascertain

this value. Six diene determinations were made on the tung oil at this Laboratory which resulted in 77.4 percent eleostearic acid content. This oil was examined in the spectrophotometer and gave a value of 147 at 270 mu. Calculation of this at 100% alpha eleostearic acid, the value of 189 was found which checks perfectly with the values reported in Ref. 7 and Ref. 8. The fact that these values check so closely is an indication of the reliability of the value given in the literature.

13. Since the triene conjugation of tung oil (alpha eleostearic acid) and that obtained from isomerization of linolenic acid is not of the same absorption, it was necessary to establish a concentration curve for isomerized linolenic acid or pseudoeleostearic acid. This acid also has the same absorption as beta eleostearic acid. From the aforementioned references as were reviewed in Ref. 9, these conjugated trienes give a maximum of 215 at 268 and also affect the 232 wave length by a value of 16. After separation and subsequent recrystallization of beta eleostearic acid, a value of 205 was obtained at this wavelength (Plate 3). Agreement in this type of compound was not as good as that obtained for the alpha acid, but since such low concentrations were necessary for this study (0.002 grams per liter), it is possible that the difference could occur through error at either laboratory. However, since a difference of ten will make an error which will be insignificant at the concentration under study, the value of 205 will be used for 100% triene.

14. From the above discussion it is evident that when the percent conjugation of a conjugated triene is to be determined when the source is linolenic acid, the value of 205 is to be used. When the triene is in tung oil or alpha eleostearic acid, the value of 189 is to be used. These concentration curves are shown in Plate 4.

15. The diene concentration curve presented greater difficulties; whereas the triene absorption was unaffected by the presence of diene, the same was not true where diene absorption was studied. There was also the doubt as to whether the compound, prepared by the bromination-debromination method, yielded a product of the same graphic structure as was present when pure linoleic acid was completely conjugated. In order to remove this doubt, another method of preparation was used to obtain the 9, 11 linoleic acid. This product was examined in the spectrophotometer (Plate 3) and was found to give a value of 119.95 at 234 mu. This compares favorably with the values reported in Ref. 9 for this compound although the value in the reference was reported for 232 mu at 120 specific alpha. Such agreement has resulted in sufficient confidence in this figure to use 120 for the specific alpha at 100% 9, 11 linoleic acid.

16. As was mentioned in the determination of diene conjugation, when conjugated trienes are present it is necessary to make correction for the interference of trienes at 234 mu. Pseudo- or beta eleostearic acid gives a value of 16 at 234 mu when one hundred percent trienes are present. It is, therefore, necessary first to determine the amount of conjugated

triene present in order to correct for the interference at 234 mu. For example, if an unknown were found to contain 20% triene, the interference at 234 mu would be 20% of 16 or 3.2. This correction must first be subtracted from the specific alpha of the diene before reference to the concentration curve (Plate 4).

17. In order to test the application of this method and as a matter of information, linseed oil was isomerized by the method previously described and samples were taken at intervals during the isomerization in order to follow its progress. The order of sampling is given in Table III.

TABLE III

ORDER OF SAMPLING FOR ISOMERIZED LINSEED FATTY ACIDS

Sample No.	Time	Temperature °C
-	1:25 PM	Start
-	1:35	135°
1	1:50	185°
2	2:05	205°
3	2:23	207°
4	2:45	205°
5	3:00	207°
6	3:36	203°
7	4:00	220°

These samples were examined in the spectrophotometer and were also analyzed by the modified Ellis-Jones Method for percent conjugation. Table IV shows the comparison of the two methods as well as the course through which the isomerization took place. Further comparison of the methods can be seen in Table V in which several commercial oils were examined.

18. It is notable from the results shown in these tables that in nearly all cases the modified Ellis-Jones Method is from 1% to 4% higher. The fact that there is at times poor checks is explained by the fact that the modified Ellis-Jones Method, by its nature, is subject to many variables and also to the errors in manipulation as well as purity of reagents.

TABLE IV

COMPARATIVE ANALYSIS OF ISOMERIZED LINSEED FATTY ACIDS

Sample	Total Conjugation (U.V.) % Diene	% Triene	% Total	Total Conjugation (Modified Ellis-Jones) % Total
1	10.00	1.00	11.00	9.6
2	32.00	10.50	42.50	45.0
3	35.50	11.25	46.75	47.0
4	35.00	10.50	45.50	46.6
5	35.50	9.75	45.25	46.0
6	35.00	9.75	44.75	-
7	35.25	10.15	45.40	49.0

TABLE V

COMPARISON OF MODIFIED ELLIS-JONES AND SPECTROPHOTOMETRIC METHODS

Sample	Spectrophotometric	Modified Ellis-Jones
Kastolene	26.75	28.81
Castung 103	26.50	29.88
Castung 403	26.75	28.46
Castung Special	28.00	28.60
Roosenol 100	22.30	22.07
Roosenol 200	4.86	4.64
Dehydrol	18.22	23.30
Isoline Fatty Acids	24.73	27.12
Isomerized Castung Fatty Acids	57.48	54.65

CONCLUSIONS AND RECOMMENDATIONS

19. The spectrophotometric method is superior to the chemical method in that (a) once the primary standards have been recorded there is no further error in the determination excepting defects in the instrument which are easily detected or checked; (b) the determination can show differentiation between diene and triene as well as total conjugation; and, (c) the time required for the determination is considerably shortened and thus affords more determinations per unit time.

20. It is recommended that the spectrophotometer be put to a more practical use in ascertaining the requirements, limitations and acceptabilities of drying oils which are used in Navy Specification protective coatings.

REFERENCES:

1. Vegetable Fats and Oils, Jamieson, 2nd Ed., monograph No. 58, pp. 398-400.

2. Bradley, T. F. and Richardson, D. Ind. and Eng. Chem. Anal. ed. Vol. 34, No. 2 (1942).

3. Kaufmann, H. P. and Baltes, J. Ber., 69, 2676 (1936).

4. Jordon, L. A., J. Soc. Chem. Ind. I, T. (1934).

5. McKinney and Jamieson, Oil and Soap 15, 30. (1938).

6. Laboratory Letters, Spencer-Kellogg & Sons, Inc.

7. Kaufman, H. P., Baltes, J. and Funke, Fette u. Seifer 45, 302 (1938).

8. Miller & Kaas, A.C.S. Meeting in St. Louis (April 1941).

9. Protective & Decorative Coatings, Mattiello, Vol. IV, pp. 388-389.

PLATE I

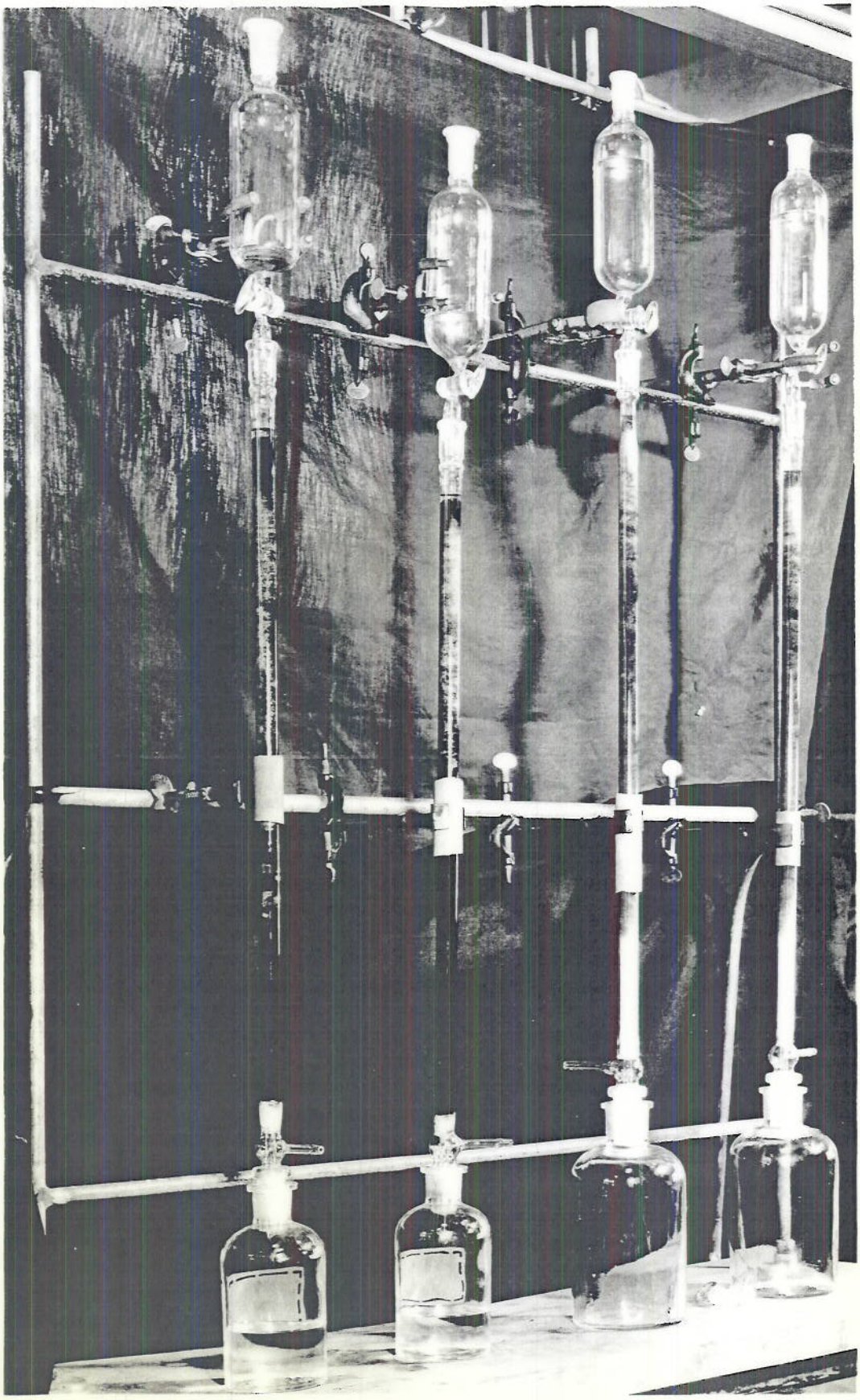

PLATE 2

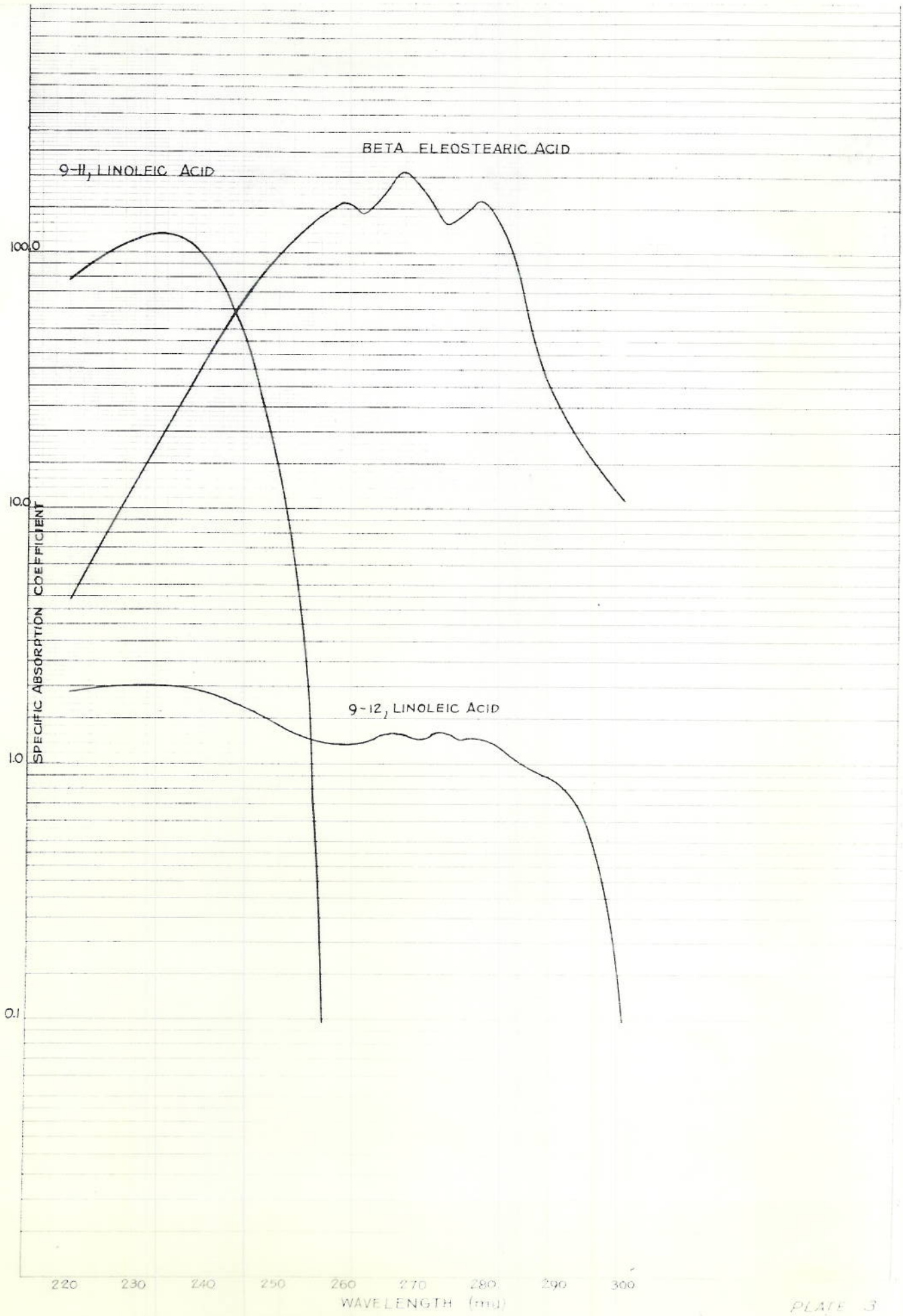
BETA ELEOSTEARIC ACID
9-11, LINOLEIC ACID
9-12, LINOLEIC ACID
100.0
10.0
1.0
0.1
SPECIFIC ABSORPTION COEFFICIENT
220
230
240
250
260
270
280
290
300
WAVELENGTH (mμ)

PLATE 3

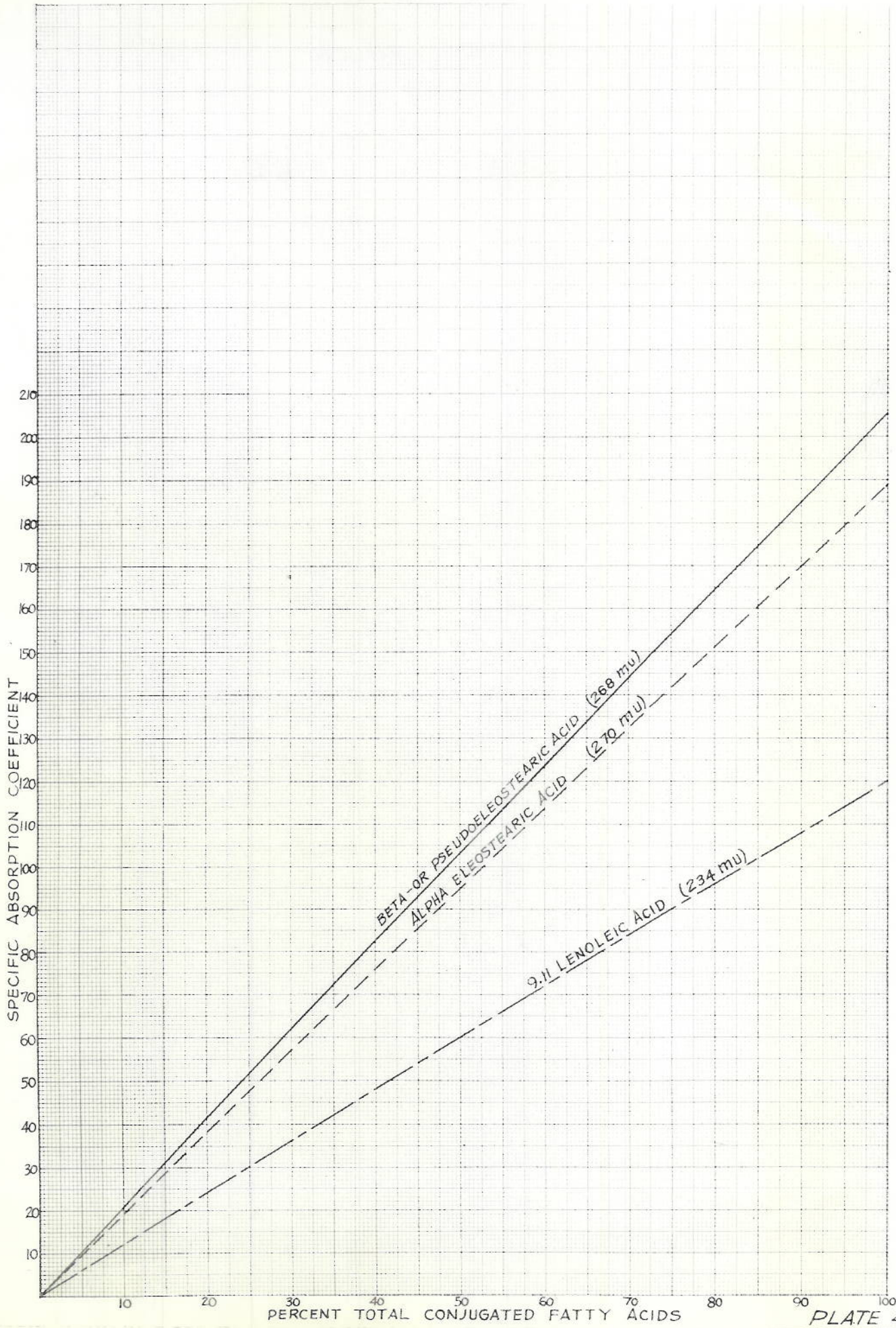
SPECIFIC ABSORPTION COEFFICIENT
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
BETA-OR PSEUDOELEOSTEARIC ACID (268 mμ)
ALPHA ELEOSTEARIC ACID (270 mμ)
9.11 LENOLEIC ACID (234 mμ)
10
20
30
40
50
60
70
80
90
100
PERCENT TOTAL CONJUGATED FATTY ACIDS

PLATE 4