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The Infrared Absorption Spectra of some Mono-unsaturated and Saturated Fatty Acids and Esters

AAGE JART

Danish Fat Research Institute, Copenhagen, Denmark

Infrared spectra (from 600 to 4 000 cm^{-1}) of 43 different fatty acids and fatty acid esters in carbon disulphide solution have been recorded. Main stress has been laid on the study of the *trans* absorption at 962 cm^{-1}, and extinction coefficients of the pure substances at the *trans* maximum have been calculated. Beer's law has been shown to apply for concentrations upto 200 g substance per liter of solution. Mention is further made of a base line method for the quantitative determination of *trans* monoene fatty acids in mixtures with saturated acids and *cis* forms of unsaturated fatty acids and fatty acid esters. Ten of the recorded infrared spectra are reproduced.

The study of the *cis-trans* isomerism of unsaturated fatty acids is of interest in connection with the industrial production of hydrogenated edible fats as well as the preparation of pure organic compounds in the laboratory. For quantitative determination of a *trans* isomer of the type RCH:CHR [1] occurring together with the corresponding *cis* isomer and the saturated compound the absorption at 960—970 cm^{-1} in the infrared spectrum may be used. The absorption is the result of a deformation vibration of the carbon-hydrogen bond; on account of this origin of the absorption band, the weight of the groups linked to the carbon atoms of the double bond has only a slight influence on the location of the band.

In 1950 the results were published of the first systematic determinations of the extinction coefficients at 965 cm^{-1} of certain fatty acids, fatty acid methyl esters and triglycerides [1,2]. The extinction values determined in these works were mainly those of four systems of "corresponding compounds", *viz.* derived from 9-octadecenoic acid, its methyl ester, the corresponding alcohol and 6-octadecenoic acid (petroselinic acid). For this purpose the term "corresponding compounds" is intended to cover a monounsaturated *cis* compound, the *trans* compound and the corresponding saturated compound; oleic acid, elaidic acid and stearic acid thus form a system of "corresponding acids".

In a work [3] from 1953, which deals exclusively with C_{18}-fatty acids, extinction coefficients are given for the oleic acid system and, in addition, for the

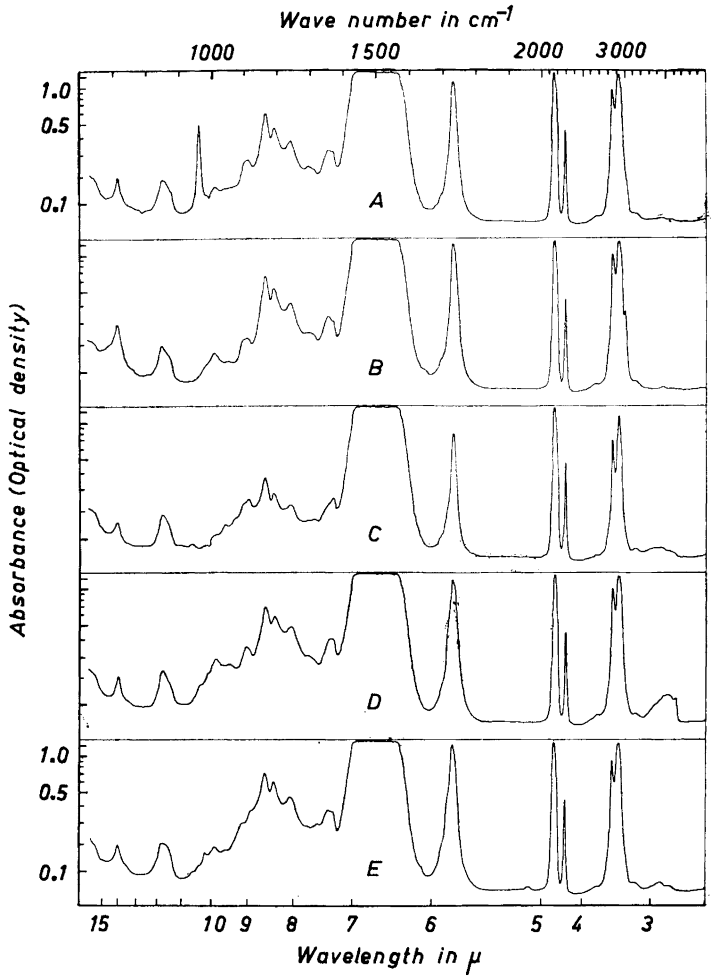

Fig. 1. Infrared spectra. (Carbon disulphide solutions; 0.0110 cm sodium chloride cell). A, Methyl brassidate (98.8 g/l); B, Methyl erucate (108.4 g/l); C, Methyl behenate (57.9 g/l); D, Methyl 12-hydroxy-stearate (102.8 g/l); E, Methyl stearolate (100.6 g/l).

two 12-hydroxy-9-octadecenoic acids (ricinoleic acid and ricinelaidic acid) and for various conjugated and non-conjugated polyene fatty acids.

In a study from 1955 of glycerides [4] mention is made of triolein and trielaidin, various butyro- and aceto-glycerides as well as tributyrin and triacetin.

A work [5] from 1956 gives extinction coefficients of the oleic acid system (in the form of acids, methyl esters and triglycerides) as well as of lauric acid, myristic acid and palmitic acid and the corresponding methyl esters. In another work [6] from 1956 mention is made of the oleic acid system, palmitic acid and linoleic and linolenic acid.

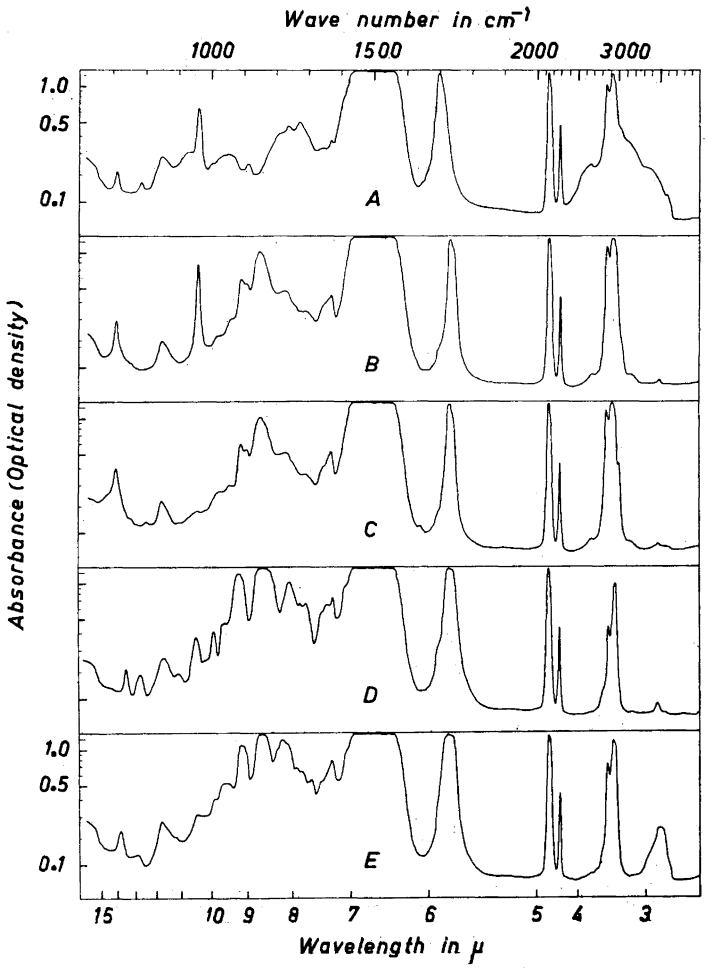

Fig 2 Infrared spectra (Carbon disulphide solutions; 0.0110 cm sodium chloride cell). A, Ricinelaidic acid (99.9 g/l); B, Tribrassidin (152.0 g/l); C, Trierucin (159.7 g/l); D, Tributyrin (116.6 g/l); E, Tricaproin (126.0 g/l).

The determination of ricinelaidic acid and its methyl ester as well as various derivatives of ricinelaidic acid is studied in two works [7,8], published in 1959. Another work [9] dealing with the oleic acid, elaidic acid, erucic acid and brassidic acid, the corresponding methyl esters and barium salts as well as a few glycerides of lower fatty acids appeared also at this time.

The aims of the present work are to perform a systematic determination of extinction coefficients at the *trans* maximum (960—970 cm^{-1}) of a series of monounsaturated and saturated fatty acids and fatty acid esters by means of a widely used spectrophotometer (Perkin-Elmer, Model 21) and to study

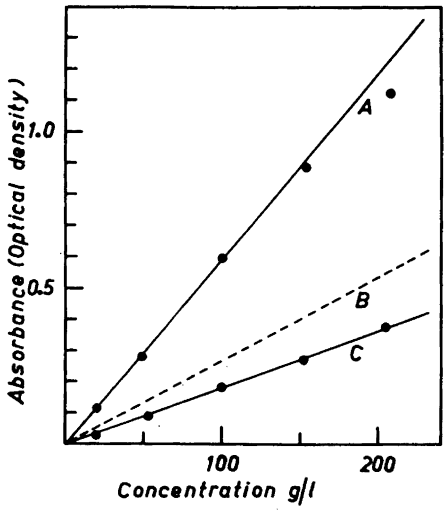

Fig. 3. Relationship between optical density and concentration in the ricinoleic acid system (0.0110 cm sodium chloride cell). A, Ricinelaidic acid; B, 12-hydroxy-stearic acid; C, Ricinoleic acid.

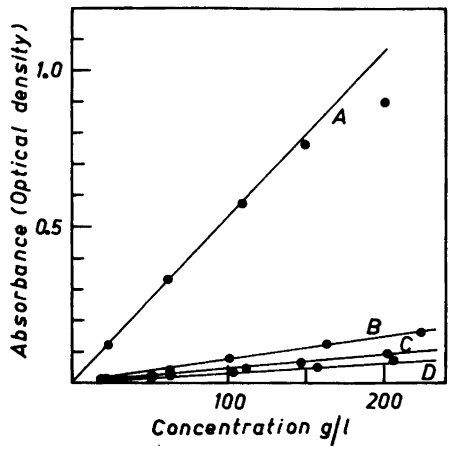

Fig. 4. Relationship between optical density and concentration in the oleic acid methyl ester system (0.0110 cm sodium chloride cell). A, Methyl elaidate; B, Methyl stearolate; C, Methyl oleate; C, Methyl stearate.

conditions in connection with the quantitative determination of *trans* monoene fatty acids with a particular view to the study of the *cis-trans* transformation which may occur during the catalytic hydrogenation of fats.

DETERMINATION OF EXTINCTION COEFFICIENTS AT 962 cm^{-1}

The examination has dealt with eight systems of corresponding compounds (Table 1) based on oleic acid and consisting of acid, methyl ester and triglyceride, on erucic acid in the form of acid, methyl ester and triglyceride, as well as on ricinoleic acid in the form of acid and methyl ester. Furthermore the methyl ester of stearolic acid (which has a triple bond in the 9,10-position) has been investigated; the results are given in connection with the oleic acid methyl ester system.

The twenty-five compounds comprised by this part of the study were examined in carbon disulphide solution. Usually, concentrations of 20, 50, 100, 150, and 200 g of the compound per 1 liter solution were applied. A 0.0110 cm sodium chloride cell was used. As the solubility of the saturated compounds in carbon disulphide is in many cases rather small, a weaker solution in a 0.114 cm sodium chloride cell has been used in these cases.

A comparison of the spectra of the *cis* compounds, *trans* compounds and saturated compounds will disclose the existence of characteristic differences (*cf.* Figs. 1 and 2 *). Unlike the *cis* compounds and the saturated compounds,

* Owing to considerations of space, it will be impossible in this publication to record the spectra of all the compounds examined.

trans compounds display a considerable absorption at 962 cm^{-1} (CH bending about the *trans* C=C group). The *cis* compounds differ from the other two groups in two ways; in the first place the absorption band at 715 cm^{-1} (CH_2 rocking) is wider, and, in the second place, an absorption band may be observed at 3 020 cm^{-1}, forming a shoulder on the broad band (C—H stretching from $CH_3 + CH_2$), which is located between 2 800 and 3 000 cm^{-1}. A further examination of this part of the spectrum should be performed by means of a fluoride prism, and the following will consequently only deal with the absorption at 962 cm^{-1}.

In the absorption spectrum of the free fatty acids there is a very broad and relatively strong band within the range 925—940 cm^{-1}. This band will always be produced by solutions of fatty acids in carbon disulphide, and it is assumed to be due to an OH-deformation vibration in the carboxyl group. As it will appear from the spectra (Fig. 2, A), this band is partially superimposed on the *trans* band at 962 cm^{-1}, and in the case of free *trans* acids the extinction at 962 cm^{-1} consequently receives contributions both from the *trans* extinction and the extinction deriving from the presence of the carboxyl group. In the ricinoleic acid system the extinction is further increased on account of the broad band with maximum at 1 010—1 015 cm^{-1} (C—O stretching).

Fig. 3 shows the optical density in the ricinoleic acid system plotted against the concentration. The relationship is seen to be rectilinear as long as $D < 0.7$. Closely corresponding pictures are obtained in the case of the oleic acid system and the erucic acid system. The corresponding extinction coefficients calculated from

$$a = \frac{\text{optical density at } 962 \text{ cm}^{-1}}{(\text{concentration in g/l}) \times (\text{width of cell in cm})}$$

are given in Table 1.

In the spectra of the methyl esters of the fatty acids (Fig. 1) the band at 925—940 cm^{-1} is seen to have disappeared completely, and in the case of esters of *trans* configuration the extinction at 962 cm^{-1} derives almost exclusively from the *trans* absorption — in the ricinoleic acid system also from the abovementioned band at 1 010—1 015 cm^{-1}. In Fig. 4 the optical density of the methyl esters of the oleic acid system has been plotted against the concentration; the corresponding graphs for the methyl esters of the two other systems have a very much similar appearance. It should again be noted that the relationship is perfectly linear as long as $D < 0.7$. The calculated extinction coefficients appear from the central column of Table 1.

The spectra of the triglycerides (Fig. 2, B and C) resemble those of the methyl esters very much. Also in the case of the *trans* isomers of these esters it applies that the absorption at 962 cm^{-1} derives chiefly from the *trans* band. The dependence of the optical density on the concentration in the case of the triglycerides of the erucic acid system appears from Fig. 5; a corresponding picture is obtained from the triglycerides of the oleic acid system. Conditions are as in the six systems previously mentioned, the relationship being linear for $D < 0.7$. The extinction coefficients are listed in the last column of Table 1;

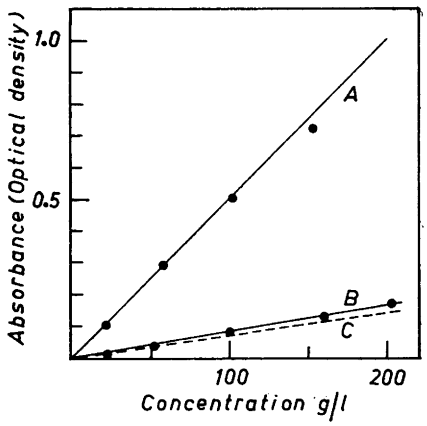

Fig. 5. Relationship between optical density and concentration in the erucic acid triglyceride system (0.0110 cm sodium chloride cell). A, Tribrassidin; B, Trierucin; C, Tribehenin.

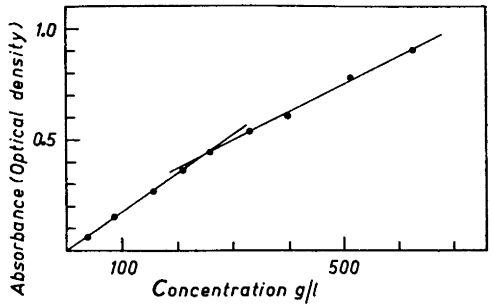

Fig. 6. Relationship between optical density and concentration for methyl elaidate (0.00353 cm potassium bromide cell).

they are somewhat higher than those of the methyl esters, but lower than those of the free fatty acids.

The phenomenon that the optical density is relatively smaller at higher concentrations than at lower concentrations, which is illustrated in Figs. 3—5, may be accounted for in two ways. It may either be the result of a considerable deviation from Beer's law, the extinction coefficient being dependent on the concentration, or the spectrophotometer may exhibit considerable deviation with regard to optical densities higher than 0.7, or both explanations may apply, producing a combined effect. To throw more light on this problem, supplementary investigations were made by means of a thinner cell (0.00353 cm KBr). These experiments showed (Fig. 6) that the relationship is rectilinear up to concentrations of 250 g methyl elaidate per liter solution; the corresponding extinction coefficient was 0.490 — a value which agrees with that found previously. Also in the concentration range 250—650 g per liter solution the relationship seemed to be linear, although the straight line did not coincide with the former, and the dispersion of the points was greater. A corresponding examination was made with respect to trielaidin, and the result corresponds closely to that given for methyl elaidate. Also with respect to ricinelaidic acid it was found that the first part of the curve was a straight line (on account of the lower solubility of this compound in carbon disulphide the shape of the last part of the curve could not be ascertained). For concentrations up to 200—250 g per liter solution no deviations from Beer's law have thus been ascertained.

EXTINCTION COEFFICIENTS OF A NUMBER OF SATURATED FATTY ACID ESTERS

When determining *trans* fatty acids in fatty acid mixtures occurring in practice, it is necessary to make allowance for other saturated acids than those

Table 1. Extinction coefficients at 962 cm^{-1}.

Compound	free acid	methyl ester	glyceride
Oleic acid	0.132	0.041	0.081
Elaidic acid	0.619	0.482	0.538
Stearic acid	0.116	0.028	0.074
Stearolic acid	—	0.066	—
Erucic acid	0.118	0.035	0 077
Brassidic acid	0.537	0.417	0.460
Behenic acid	0.102	0.034	0.067
Ricinoleic acid	0.166	0.094	—
Ricinelaidic acid	0.540	0.460	—
12-Hydroxy-stearic acid	0.242	0.110	—

previously mentioned. Such fatty acids are present in large quantities in a number of natural fats (for instance in coconut oil and consequently in margarine fats) and in certain synthetic triglycerides. A systematic examination of the extinction coefficients at 962 cm^{-1} of the most frequently occurring saturated fatty acid esters was made, and the results are summarized in Table 2. As will be seen from the table, the extinction coefficients of the methyl esters from C_6 decrease with increasing number of carbon atoms in the fatty acid. In the triglyceride series the extinction coefficients decrease steadily with increasing number of carbon atoms, while the molecular extinction coefficient ($= M \times a$, where M is the molecular weight of the triglyceride) is fairly constant (67 ± 9). In the case of triacetin and tributyrin (Fig. 2, D) there are pronounced absorption maxima very near 962 cm^{-1}, *viz.* at 954 cm^{-1} ($a = 0.345$) and at 957 cm^{-1} ($a = 0.260$), while in the case of tricaproin (Fig. 2, E) only an indistinct maximum at 959 cm^{-1} can be observed, and in the case of the higher members of the series the maximum cannot be distinguished from the background.

THE BASE-LINE TECHNIQUE

To be able to determine the content of a *trans* fatty acid in a mixture of fatty acids by means of its extinction coefficient, it is necessary to have a fairly accurate knowledge of the accompanying components of the mixture, which must be determined by gas chromatography or another method. Since the spectra of *cis* fatty acids and of saturated acids resemble each other very much within the range about 962 cm^{-1}, the *trans* absorption may be separated from the "background" absorption by means of a suitable base line. This line may either be drawn in such a way that it approximates the spectrum of the corresponding *cis* isomer, or a straight line may simply be traced as shown in Fig. 7 for a number of *trans* compounds. The distance, D *, from this base line to the peak of the maximum at 962 cm^{-1} corresponds to pure *trans* absorption, and the relationship between this value and the concentration is in principle the same as that found with respect to the total absorption, D, at 962

Table 2. Extinctions at 962 cm^{-1} of methyl esters and triglycerides of saturated acids.

Compound	Methyl ester	triglyceride	
	a	a	ε
Acetic acid	0.036	0.290	63
Butyric acid	0.024	0.246	74
Caproic acid	0.062	0.189	73
Caprylic acid	0.046	0.124	58
Capric acid	0.049	0.116	64
Lauric acid	0.035	0.097	62
Myristic acid	0.037	0.082	59
Palmitic acid	0.031	0.076	61
Stearic acid	0.028	0.074	66
Arachidic acid	0.030	0.078	76
Behenic acid	0.034	0.067	71

cm^{-1}. Fig. 8 shows the curve plotted for tribrassidin; with respect to the remaining seven compounds the curves correspond closely to the *trans* fatty acid curves shown in Figs. 3—5. The curves are straight lines, but also in this case the higher values of the optical density are too small. From the magnitude D^* it is possible to calculate a corresponding *trans* extinction coefficient, a^*, from:

$$a^* = \frac{D^*}{(\text{conc. in g/l}) \times (\text{width of cell in cm})}$$

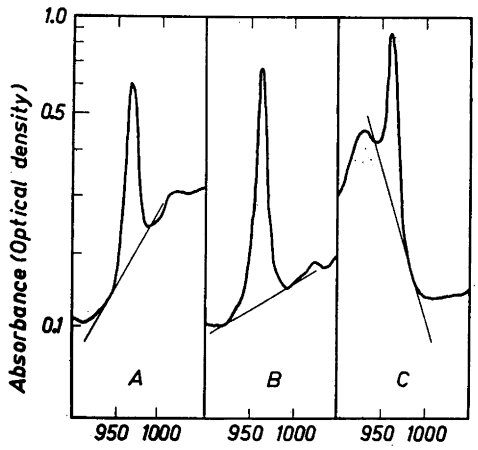

Fig. 7. Tracing of base line for a number of *trans* compounds. A, Methyl ricinoleate (108.6 g/l); B, Trielaidin (105.3 g/l); C, Brassidic acid (147.3 g/l). Abscissas: Wave number in cm^{-1}.

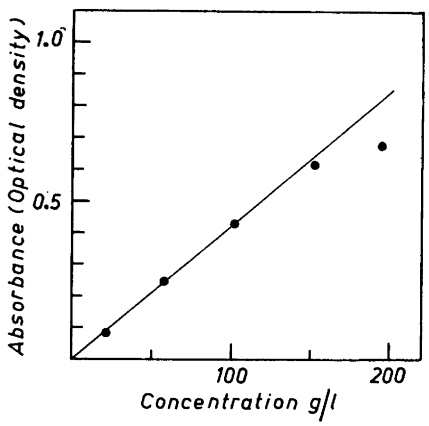

Fig. 8. Relationship between optical density and concentration for brassidic acid triglyceride (base line method, 0.0110 cm sodium chloride cell).

Table 3. Pure *trans* absorptions at 962 cm^{-1}.

Compound	Absorptivity a *	Molar absorptivity ε *
Elaidic acid	0.445	125.9
Brassidic acid	0.376	127.1
Methyl elaidate	0.423	125.4
Methyl brassidate	0.355	125.2
Trielaidin	0.467	413.5 (138)
Tribrassidin	0.387	407.9 (136)
Ricinelaidic acid	0.354	110.6
Methyl ricinelaidate	0.340	101.5

The calculated values are listed in the first column of Table 3. The last column lists the corresponding molecular values, ε *, which are obtained by multiplying values of a * by the corresponding molecular weights. It will be seen that in the case of the simple fatty acids, elaidic acid and brassidic acid and their methyl esters, the molecular value may be taken to be 126. The values for the glycerides are somewhat higher (138 and 136, respectively, calculated per molecule of fatty acid), while those for the hydroxy-substituted compounds are somewhat lower.

In the case that a great precision is not necessary it thus seems favourable to use the base-line technique.

THE PURITY OF THE SUBSTANCES USED

The preparation of the fatty acids and fatty acid esters used in the present investigation is described under the heading Experimental. All *trans* isomers were prepared to such a grade of purity that it was not possible by gas chromatography or other methods to demonstrate the presence of impurities. The purity of the saturated acids is about 99.5 %, which is sufficient for the present purposes as the impurities in this case consist of closely related substances with a corresponding absorption at 962 cm^{-1}. The purity of ricinoleic acid is 99 %, that of oleic acid and erucic acid about 97—98 %, and the same applies to stearolic acid. None of these deviations from 100 % purity should cause any significant alteration of the numerical values of the extinction coefficients. In the case of the triglycerides of some of the lower acids (fats which were originally prepared for feeding experiments) the contents of impurities were determined by gas chromatography, and the extinction coefficients were corrected accordingly. A little content of free hydroxy groups in some of these triglycerides was noticed, but in this connection it does not influence the extinction values.

Direct comparison of extinction values determined by means of different spectrophotometers is not possible, since the individual instruments may differ considerably with regard to scattered radiation, slit width, *etc.* The numerical values found in the present work do, however, agree well with the results of most of the works mentioned in the above. The extinction coefficient values found for the *trans* isomers were, however, about 10 % higher than the results generally given in the literature. The extinction coefficient values given in the following are believed to be in most cases accurate to ± 2 %.

EXPERIMENTAL

Equipment. A Perkin-Elmer spectrophotometer, model 21, with sodium chloride prism was used without any reference cell. The settings used were: speed, 6; automatic suppression, 6; gain, 5.3; intensity, 0.32 A; response, 1; resolution, 927; and slit width at 962 cm^{-1}, 120 μ. Alteration of the speed from 6 to 3 gave no significant alteration of the results.

Cells. The thickness of the 0.0110 cm sodium chloride cell was measured by the interference method. The thickness of the 0.00353 cm potassium bromide cell could not be measured in this way; it was measured by means of pure benzene. The thick cell (0.114 cm, sodium chloride) was measured by means of solutions of fatty acid esters in carbon disulphide.

Determination of extinction coefficients. A sample of the compound under examination was weighed in a calibrated volumetric flask and dissolved in carbon disulphide (Merck, analytical grade). The temperature was 24°C.

I. *Oleic acid.* Olive oil was converted into methyl esters by shaking at 60°C with 1.6 times the theoretical quantity of methanol in which 0.5 % of sodium hydroxide was dissolved; the mixture was set aside for one hour at 60°C and allowed to stand overnight at room temperature. The upper phase was then separated and distilled *in vacuo*. Saturated acids were removed by setting aside the methyl oleate for one week at −40°C in acetone (10 ml per g of methyl ester). Crystallization was effected at −60°C by means of dry ice with gentle stirring; the resulting precipitate was isolated, and oleic acid was recovered by saponifying with 2 N ethanolic potassium hydroxide and acidifying with 50 % sulfuric acid. Linoleic acid was removed from the resulting free acid by recrystallizing three times from acetone at −40°C. The precipitate was evaporated to dryness *in vacuo*. The purity was determined by alkali-isomerization, determination of iodine value and gas chromatography [10].

II. *Elaidic acid.* A commercial product (B.D.H.) was recrystallized three times from three times its volume of 99.9 % ethanol by being allowed to stand at 5°C. Melting point, 43.8−44.0°C.

III *Stearic acid.* A commercial product (B.D.H.), which was found by gas chromatography to contain 96 % stearic acid and 4 % palmitic acid, was fractionated on a 0.6 m packed column (with 1/8 in. Dixon rings). Melting point, 68.6°C.

IV. *Erucic acid.* Rape seed oil was converted into methyl esters as described under I. The esters were carefully fractionated by vacuum distillation, and the C_{22} fraction was allowed to crystallize from acetone at low temperature in a similar manner to that described in the case of methyl oleate under I. The test for purity was performed as in the case of oleic acid.

V. *Brassidic acid.* A commercial product (California Corporation for Biochemical Research) was recrystallized six times from 99.9 % ethanol (at a ratio of 1:1.5) by being allowed to stand at 5°C. Melting point, 59.0−59.2°C.

VI. *Behenic acid.* A technical grade product was converted into methyl esters by means of methanol and sulfuric acid and fractionated on a 0.6 m packed column (Dixon rings). A suitable fraction was recrystallized three times from 96 % ethanol (at a ratio of 1:10) at room temperature. Melting point, 79.8°C.

VII. *Ricinoleic acid.* Castor oil was converted into methyl esters as described under I. The methyl esters were fractionated *in vacuo*, and one fraction which, by gas chromatography, was found to be pure was saponified by means of ethanolic potassium hydroxide

and acidified with 50 % sulfuric acid. Test for purity as described in the case of oleic acid (I).

VIII. *Ricinelaidic acid.* Castor oil was saponified and acidified, and mercury and strong nitric acid were allowed to act on the free fatty acids with stirring. The mixture was washed with water and recrystallized six times from light petroleum at room temperature. Melting point, 50.4°C.

IX. *12-Hydroxy-stearic acid.* Ricinoleic acid methyl ester (*cf.* VII) was hydrogenated with palladium catalyst (10 % Pd on activated carbon) for 8.5 h at 65° in methanol solution; in this way 60 % of the double bonds were hydrogenated. The resulting product was saponified by addition of excess of 2 N aqueous potassium hydroxide and acidified with 50 % sulfuric acid to precipitate the fatty acids. Following two recrystallizations from 96 % ethanol, the melting point of the acids was 76°C. The acids were esterified with methanol and sulfuric acid and fractionated by vacuum distillation. One fraction, with melting point at 49°C, was recrystallized twice from 99.9 % ethanol at 5°C. Melting point, 56.0—56.3°C. The ester was saponified with ethanolic potassium hydroxide and acidified with sulfuric acid. Melting point of the acid, 79.4°C.

X. *Methyl acetate.* A commercial product (B.D.H.) was used.

XI. *Methyl butyrate.* A commercial product was ascertained by gas chromatography to be sufficiently pure.

XII. *Methyl caproate.* Technical grade caproic acid was esterified with methanol and sulfuric acid and fractionated on a 1 m spinning-band column. Tested for purity by gas chromatography.

XIII. *Methyl caprylate.* Prepared in the same way as XII.

XIV. *Methyl caprate.* Prepared in the same way as XII.

XV. *Methyl laurate.* Prepared in the same way as XII.

XVI. *Methyl myristate.* Prepared in the same way as XII.

XVII. *Methyl palmitate.* Prepared in the same way as XII.

XVIII. *Methyl oleate.* Prepared from I by esterification with methanol and sulfuric acid.

XIX. *Methyl elaidate.* A, Prepared from II by esterification with diazomethane [11]. B, Another quantity was prepared by alcoholysis of trielaidin (XXXVIII B) with methanol (according to I) and vacuum distillation of methyl elaidate.

XX. *Methyl stearate.* Prepared from III by esterification with methanol and sulfuric acid.

XXI. *Methyl stearolate.* Prepared according to *Org. Syntheses* [12] by bromination of methyl oleate and treatment of the product obtained with potassium hydroxide and *n*-amyl alcohol. The mixture was acidified with hydrochloric acid to yield the acid which was recrystallized several times from 70 % ethanol, followed by esterification with methanol and sulfuric acid.

XXII. *Methyl arachinate.* Arachidic acid, 95 % pure, war recrystallized three times from 95 % ethanol and esterified with diazomethane [11].

XXIII. *Methyl erucate.* Prepared from IV by esterification with methanol and sulfuric acid.

XXIV. *Methyl brassidate.* Prepared from V by esterification with diazomethane [11].

XXV. *Methyl behenate.* Prepared from VI by esterification with diazomethane [11].

XXVI. *Methyl ricinoleate.* Intermediate from the preparation of VII.

XXVII. *Methyl ricinelaidate.* Prepared from VIII by esterification with diazomethane [11].

XXVIII. *Methyl 12-hydroxy-stearate; cf.* IX. Melting point, 56.0—56.3°C.

XXIX. *Triacetin.* Commercial product (from R de H). Tested for purity by gas chromatography.

XXX. *Tributyrin.* Commercial product (from B.D.H.). Fractionated by vacuum distillation. Tested for purity by gas chromatography.

XXXI. *Tricaproin.* Technical grade caproic acid (R de H) was esterified with methanol and sulfuric acid. After washing with sodium bicarbonate solution and drying with anhydrous sodium sulfate, the methyl ester was fractionated by distillation. Interesterification of methyl caproate and triacetin was effected by heating for 5 h to 80°C with 95 % of the theoretical quantity of neutralized and dried triacetin (R de H) to which had been added 1 % sodium methylate dissolved in methanol; the methyl acetate formed was removed during the process by suction with a water-jet pump. Excess methyl ester

was subsequently removed by passing steam through the triglyceride at 80°C and 20 mm Hg. The resulting triglyceride was treated with 1 % activated carbon and filtered. Composition: 99.5 % C_8; 0.5 % C_8.

XXXII. *Tricaprylin.* Prepared from technical grade caprylic acid (R de H) in the same way as XXXI. Composition: 98.5 % C_8; 1.5 % C_{10}.

XXXIII. *Tricaprin.* Prepared from technical grade capric acid (B D. H) in the same way as XXXI. Composition: 3.1 % C_8; 93.5 % C_{10}; 3.4 % C_{12}.

XXXIV. *Trilaurin.* Prepared from technical grade lauric acid by esterification with 98 % glycerol *in vacuo* at 200°C for 5 h with 0.2 % stannous chloride as catalyst. Washed with aqueous sodium carbonate solution and dried with kieselguhr. Composition: 0.6 % C_8; 10.7 % C_{10}; 86 % C_{12}; 2.7 % C_{14}.

XXXV. *Trimyristin.* Prepared from 98 % myristic acid (B.D.H.) by esterification with 95 % glycerol *in vacuo* at 200°C for 5 h with 1 % stannous chloride as catalyst. Washed with sodium bicarbonate solution and water. Recrystallized three times from benzene. Melting point, 56.8°C.

XXXVI. *Tripalmitin.* Prepared from palmitic acid (B.D.H.) in the same way as XXXV. Recrystallized three times from benzene. Melting point, 65.3°C.

XXXVII. *Triolein.* Prepared from I by esterification with 90—95 % glycerol at 125°C for 8 h, passing nitrogen through the solution and using 1 % *p*-toluene sulfonic acid as catalyst. The mixture was dissolved in two volumes of petroleum ether, washed with two portions of 70 % ethanol, the first containing potassium hydroxide for the purpose of removing free acids, and subsequently with water. Triolein was finally crystallized from acetone (1 g of triglyceride per 10 ml) at −40°C and evaporated to dryness *in vacuo*.

XXXVIII. *Trielaidin.* A, Prepared from II by esterification in the same way as XXXV. Recrystallized several times at 5°C from ethyl ether. Melting point, 42.9—43.2°C. B, Another batch equally pure was prepared from a product obtained from olive oil which was treated with sodium nitrite and nitric acid, the resulting product being washed with water and recrystallized five times at 5°C from ethyl ether.

XXXIX. *Tristearin.* Prepared from III in the same way as XXXV. Melting point, 72.6°C.

XL. *Triarachin.* Prepared from arachidic acid (*cf.* XXII) in the same way as XXXV. Recrystallized three times from benzene. Melting point, 76.9°C.

XLI. *Trierucin.* Prepared from IV by esterification with glycerol as described in the case of XXXVII.

XLII. *Tribrassidin.* Prepared from V by esterification as described in the case of XXXV. Recrystallized five times from ethyl ether at 5°C. Melting point, 58°C.

XLIII. *Tribehenin.* Prepared from VI by esterification as described in the case of XXXV. Recrystallized three times from benzene. Melting point, 81.6°C.

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