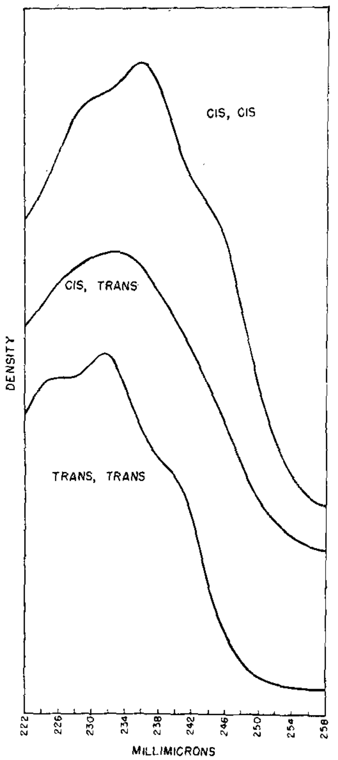

FIG. 4. Ultraviolet absorption curves of conjugated linoleate isomers.

produced decreased values for k. The results of equilibration are shown in Table II. Percentage conjugation was calculated on the basis of the *cis, trans* isomer as 100% conjugated by dividing the equilibrium values by 102.4.

The isomerization was done on the solutions used to measure absorption at concentrations suitable for accurate measurements by the instrument.

The agreement between the infrared and ultraviolet values are excellent for the *cis, cis* and *trans, trans* compounds. On the dehydrated castor oil ester fraction and the alkali conjugated linoleate, the infrared values are higher. In the former case, at least, this is probably attributable to the isolated *trans* structure, which has a peak at 10.3 μ and would contribute to the 10.13 μ band.

TABLE II

Compound	mμ max.	k, before equil.		k, equil. 231.5 mμ	Conj.	
		Cary	D.U.		U.V.	I.R.
					%	%
Cis, trans	233.0	93.7	93.9	102.4	100	100
Trans, trans	231.5	103.1	103.6	97.3	95	98
Cis, cis	235.5	80.8	......	90.9	89	91
Deh. c.o.	232.0	67.7	......	74.0	72	82
Alk. conj.	233.0	79.5	......	88.6	87	93

The equilibrated *cis, trans* isomer, assumed to be 100% conjugated, has a value of $k_{231.5} = 102.4$. The calculated value, by adding 64% of the corrected $k_{231.5}$ of the unisomerized *trans, trans* isomer plus 32% of $k_{231.5}$ of the unisomerized *cis, trans* isomer, plus 4% of $k_{231.5}$ of the unisomerized *cis, cis* isomer, is k = 102.8 (if the conjugated *trans, trans* isomer is assumed to be 95% pure) or k = 100.6 if the *trans, trans* isomer is assumed to be 98% pure.

Discussion

In the absence of much isolated *trans*, the iodine-equilibrated mixture should afford a convenient infrared spectrophotometric method for analyzing mixtures of conjugated diene isomers for total conjugation. Since it is reported that iodine does not cause conjugation of isolated double bands under similar conditions (2), it should be applicable to mixtures of conjugated diene isomers with *cis* nonconjugated dienes. It is spectrally somewhat analogous to the chemical "pandienzahl" of Von Mikush (3). Ultraviolet absorption on the equilibrated mixture would give total conjugation without interference by *trans* isomers. For determination of *cis, trans* and *trans, trans* conjugated isomers (in the absence of much isolated *trans*) infrared absorption is useful.

Summary

Infrared and ultraviolet studies have shown that the three geometrically isomeric types of conjugated linoleates (*cis, cis*; *cis, trans*; and *trans, trans*) are readily equilibrated by dilute iodine and light. Infrared shows that the equilibrium is at 32% *cis, trans* and 64% *trans, trans* isomer. Probably no more than 5–10%, if any, *cis, cis* isomer exists at equilibrium. The equilibrated mixture can be used to determine total conjugation in mixtures of conjugated geometric isomers by either infrared or ultraviolet absorption.

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Fractionation and Glyceride Composition of Fats[1, 2, 3]

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THIS PAPER deals with a new method of correlating fractionation data for natural fats, which provides further information on the glyceride composition of the fats. In particular it relates to the distribution of the unsaturated fatty acids among the glyceride types GS_2U, GSU_2, and GU_3.

The present work was begun when it was noted that a direct relation existed between the linolenic acid content and iodine value for fractions obtained from rapeseed oil. Such a regular relation must stem from some definite pattern for the separation of the glycerides on fractionation, and the form of the rela-

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[1] From a thesis submitted by C. G. Youngs to the Faculty of Graduate Studies, University of Saskatchewan, in partial fulfilment of the requirements for the degree of doctor of philosophy.

[2] Presented at fall meeting, American Oil Chemists' Society, Cincinnati, O., September 30–October 2, 1957.

[3] Issued as N.R.C. No. 4779.

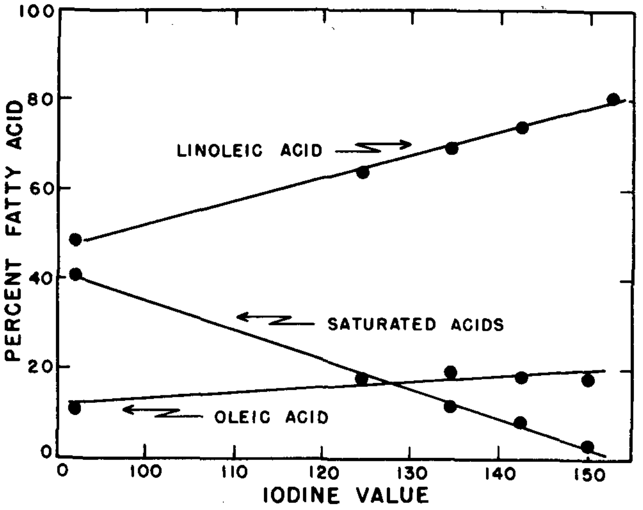

FIG. 1. Fatty acid content *versus* iodine value for sunflower oil fractionated by Craig (1).

tion must ultimately be determined by the amounts and types of the various glycerides present. Rapeseed oil contains a relatively large number of fatty acids varying both in chain length and degree of unsaturation, and the resulting mixture of glycerides is too complex to be suitable for further analysis of this type.

Examination of fractionation data in the literature for less complex fats showed that similar direct relations existed here. For example, Craig (1) has divided sunflower oil into five fractions by low-temperature crystallization from acetone and determined the iodine values and fatty acid compositions of the fractions. These data are plotted as the content of the various fatty acids *vs.* iodine value in Figure 1. For each of the fatty acids there is a direct relation between the iodine value of the fractions and the percentage of fatty acid in the fractions.

Such direct relations would only be expected if fractionation led to a division of the oil into components, the iodine values and fatty acid compositions of which were such that they fall on the same lines as those for the experimental fractions. If the components into which the oil was divided did not have these properties, a scattering of the points would be expected, representing fractions rich in some particular component.

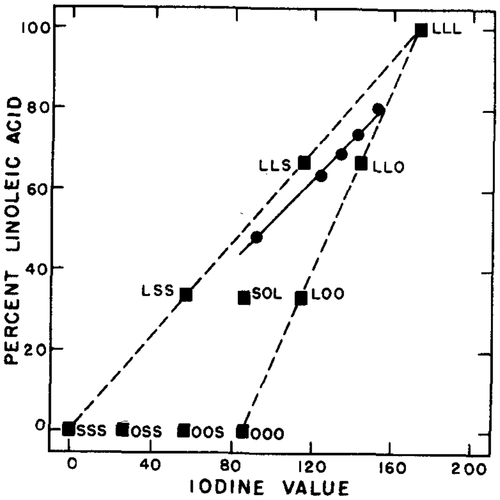

FIG. 2. Fractions and component glycerides of sunflower oil. ● Fractions obtained by Craig (1), ■ component glycerides, S—saturated acids, O—oleic acid, L—linoleic acid.

The possible glycerides present in the oil do not give points lying on the lines joining the experimental points. This is illustrated in Figure 2, in which the linoleic acid content of the fractions from sunflower oil are replotted against iodine value along with points representing the possible glycerides present in the oil. It would therefore appear that fractional crystallization does not result in separations based on individual glycerides but rather in separations based on certain groups of glycerides. The properties of these groups must be such that points representing them lie on the same lines as the experimental fractions.

Although the approach taken here is new, the idea that fractional crystallization of fats leads to a division of glycerides into groups is not new. Hilditch (2), Longenecker (3), and Riemenschneider *et al.* (4, 5) have assumed the glycerides to be divided into groups on the basis of their saturated acid content. Doerschuk and Daubert (6), on the other hand, assumed division on the basis of iodine value. This latter method of grouping was also assumed by Dutton and Cannon (7) and by Scholfield and Hicks (8) for the distribution of oils between two solvents in the Craig apparatus.

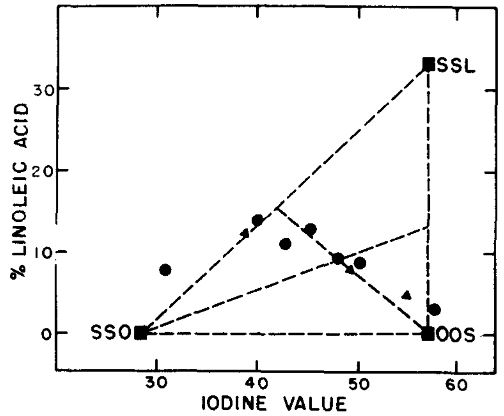

FIG. 3. Fractions from mixture of oleodistearin (SSO), linoleodistearin (SSL), and stearodiolein (OOS). ● Fractions crystallized from acetone, ▲ fractions crystallized from Skellysolve F, ■ glycerides in mixture.

It seems unlikely that either of these factors would be solely responsible for the solubility characteristics of the glycerides. One factor may be sufficiently predominant however to obscure the effect of the other. Which, if either, of these factors is predominant may be determined by fractionation of known mixtures of synthetic glycerides. A mixture of oleodistearin, linoleodistearin, and stearodiolein contains two glycerides with the same saturated acid content and two with the same iodine value. Fractionation of such a mixture should clearly distinguish between the two factors.

The above three glycerides were therefore synthesized, and a mixture of the three was fractionated by low temperature crystallization from acetone and from Skellysolve F (petroleum solvent boiling range 35–58°C.). The results of these crystallizations are shown in Figure 3. If the glycerides were divided on the basis of their iodine value, the oleodistearin would be separated from the other two and the fractions would lie on a line through oleodistearin and the original mixture. If the saturated acid content of the glycerides were the determining factor, the stearodiolein would be separated from the other two and the fractions would lie on a line through stearodiolein and the original mixture. The points representing the experimental fractions lie very close to this latter line, indicating that the saturated acid content of the glycerides is the predominant factor in determining their relative solubilities.

In complex mixtures, such as natural fats, there may be complicating factors such as mutual solubility not encountered in the above simple mixture. A synthetically prepared "random" mixture of the possible glycerides of stearic, oleic, and linoleic acids was therefore prepared, and the mixture was fractionated by low-temperature crystallization from acetone. The results of these fractionations are shown in Figure 4. The amounts of the various glycerides in the mixture were calculated on the basis of mathematical probability from the relative amounts of the three acids. The glycerides were then grouped according to their saturated acid content and according to their iodine value. The aggregate iodine values and linoleic acid contents of each group were then calculated and points representing them plotted in Figure 4.

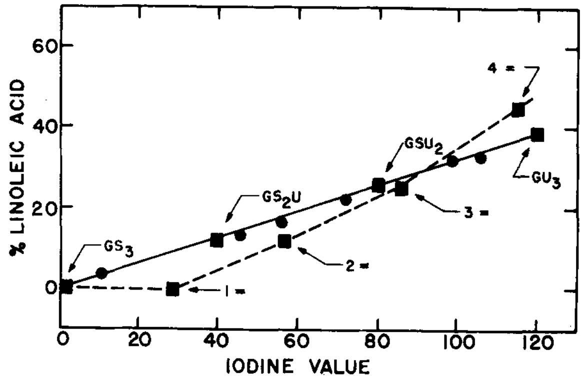

Fig. 4. Fractions from random mixture. ● Fractions crystallized from acetone, ■ glyceride groups, 1=, 2=,3=, etc., refer to total number of double bonds in the glycerides.

Points representing the groups based on saturated acid content are joined by a solid line. Points representing the groups based on iodine value are joined by a broken line. The points representing the fractions lie, within experimental error, on the solid line. It therefore appears that fractional crystallization separates glycerides on the basis of their saturated acid content.

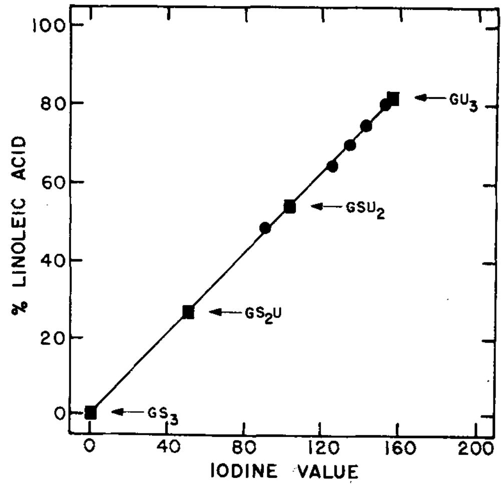

Fig. 5. Fractions and glyceride groups for sunflower oil. ● Fractions obtained by Craig (1), ■ glyceride groups.

Returning then to the fractional crystallization of sunflower oil, the aggregate fatty acid composition and iodine values of each of the four glyceride types in the oil must be such that points representing the four types lie in a single straight line on a plot of the content of a given fatty acid *vs.* iodine value. This would be the case if the relative proportions of the various unsaturated acids in each type were the same. On the basis of this assumption the iodine values and linoleic acid contents of the four glyceride types were calculated for the sample of sunflower oil fractionated by Craig (1). Points representing the glyceride types and the experimental fractions are plotted in Figure 5. All the points do, in fact, fall along a single straight line.

Figure 6 shows a similar plot of the data of Riemenschneider, Swift, and Sando (4) for the fractionation of cottonseed oil. The linoleic acid content and iodine values of the glyceride types were calculated by assuming a constant ratio between the unsaturated acids. Here again the experimental points and the calculated points for the glyceride types lie on a single straight line.

Figure 7 is the same type of plot for beef tallow. The experimental data are those of Riemenschneider, Luddy, Swain, and Ault (5). Here the content of oleic acid is plotted *vs.* iodine value. The major component acid was plotted for each of the fats as it shows the widest variation and is least subject to analytical errors. As before, experimental and calculated points fall on a single line.

It therefore appears that in at least these three fats the relative proportions of the unsaturated acids are constant throughout the glyceride types GS$_2$U, GSU$_2$, and GU$_3$, *i.e.*, there is no specificity for the location of a particular unsaturated acid with either the monosaturated or disaturated glycerides. For

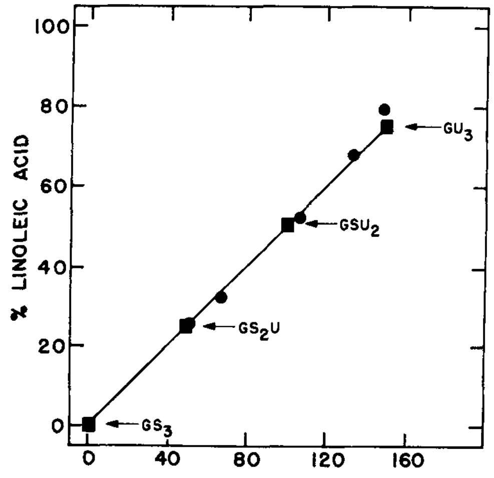

Fig. 6. Fractions and glyceride groups for cottonseed oil. ● Fraction obtained by Riemenschneider *et al.* (4), ■ glyceride groups.

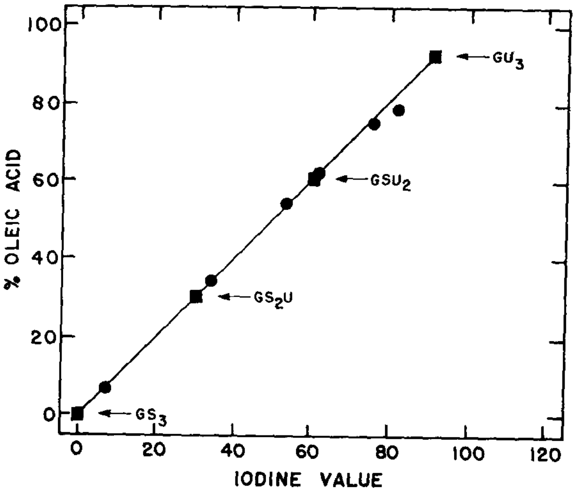

Fig. 7. Fractions and glyceride groups for beef tallow. ● Fraction obtained by Riemenschneider *et al.* (5), ■ glyceride groups.

example in sunflower oil, which contains only oleic and linoleic acids as the unsaturated acids, the ratio of oleodisaturated glycerides to linoleodisaturated glycerides is the same as the ratio of oleic acid to linoleic acid in the whole oil. This type of correlation gives no indication whether the disaturated glycerides are symmetrical, unsymmetrical, or a mixture of the two isomers. Neither can any conclusion be drawn as to the relative amounts of the various glyceride types. Since the glyceride types and experimental fractions all lie on a single straight line, it cannot be assumed that, because a fraction lies between two glycerdie types, it is composed of only those two types. Such a fraction could, and quite possibly does, contain some of all four glyceride types. However, if a fraction is obtained which lies between GS_3 and GS_2U, the fraction must contain some GS_3. Similarly if a fraction lies between GU_3 and GSU_2, some GU_3 must be present.

This might all be summed up by saying that in the three natural fats tested, having once located the saturated acids on the glycerol molecules, the unsaturated acids appear to be distributed without any specificity among the remaining positions. This is in accord with either a "complete random" or "restricted random" distribution and does not preclude the possibility that only certain of the possible positional isomers may be present in natural fats. It does however rule out an "even" distribution as this implies a certain specificity for the location of the various unsaturated acids among the glyceride types. This is illustrated in Figure 8, in which the points representing the glyceride types calculated on the basis of an even distribution are shown along with the experimental fractions for sunflower oil. The calculated and experimental points no longer lie on a single line.

So far we have only dealt with fractionation by crystallization. Dutton and Cannon (7), on fractionating linseed oil by distribution between two solvents, concluded that they had obtained a separation of the glycerides on the basis of iodine value and that the amounts of these glycerides agreed with a random distribution. To see if this agrees with the present method of correlation, the glycerides in linseed oil, as calculated by Dutton and Cannon for a random distribution, were grouped according to their iodine value and according to their saturated acid content. These two calculated sets of groups are plotted as percentage of linolenic acid *vs.* iodine value along with points representing the experimental fractions in Figure 9. In the figure the groups on the basis of saturated acid content have been joined by a solid line and those on the basis of iodine value by a broken line. The experimental fractions do indeed fall along this latter line. The manner in which glycerides are divided is apparently different for crystallization from a single solvent than it is for distribution between two solvents. If this is correct, fractionation of a particular fat by the two methods would give a cross correlation for the relative amounts of the various chemically distinguishable glycerides. This would be extremely interesting for a fat such as cacao butter, which Kartha (9) has shown does not follow a completely random distribution pattern.

Experimental

The three fatty acids required for the synthetic glycerides were prepared from vegetable oils. The oils were converted to methyl esters and distilled to give a fraction containing only C_{18} acids. The desired acids were then separated from these fractions. Stearic and oleic acid were obtained as the individual acids, but because of the difficulties involved no attempt was made to obtain linoleic acid as such. Instead a mixture of linoleic and oleic acids was used in the synthesis since the desired mixture of glycerides contained both of these acids in combination with distearin. The stearic acid had a m.p. of 69.2°C., the oleic acid had an I.V. of 89.6, and the mixture of 23.1% oleic and 76.9% linoleic acid had an I.V. of 160.0.

The preparation of glycerides containing two different acids involves blocking one or two of the hydroxyls of the glycerol, adding one acid radical, removing the blocking agent, and adding the other acid radical. The acid radicals were added as the acid chlorides, which were prepared as described in an earlier publication (10).

Distearin was prepared by using the trityl group as the blocking agent (11). An 80% yield of re-

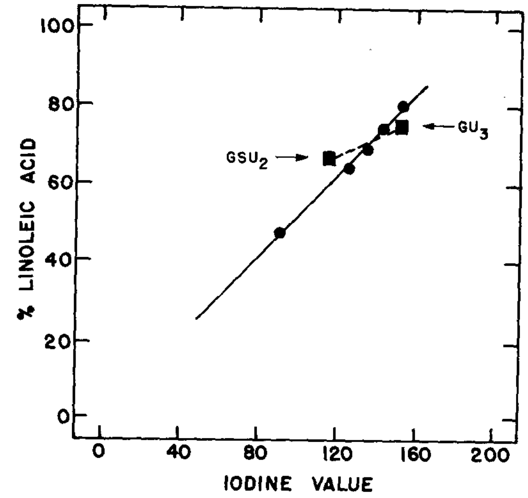

Fig. 8. Fractions and glyceride groups for sunflower oil. ● Fractions obtained by Craig (1), ■ glyceride groups for an "even" distribution.

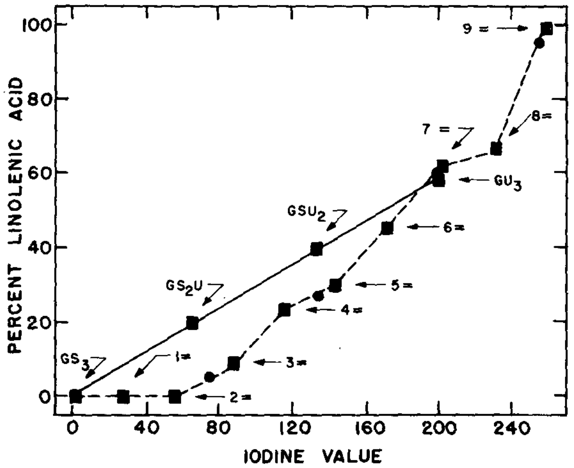

Fig. 9. Fraction and glyceride groups for linseed oil. ● Fractions obtained by Dutton and Cannon (7), ■ glyceride groups for a "random" distribution, 1=, 2=, etc., refer to the total number of double bonds in the glyceride.

crystallized product was obtained, having a melting point of 76 to 79°C. This procedure reportedly results in the symmetrical 1,3-distearin, for which melting points as high as 80°C. have been reported (12). Recent work by Verkade and Van Lohuizin (13) indicated that a mixture of 1,3- and 1,2-distearin is obtained. This was verified by X-ray diffraction patterns for the sample obtained here. Lines corresponding to the reported spacing (14) for both the symmetrical and unsymmetrical distearins were present. This possibly accounts for the low melting point obtained. Determination of the hydroxyl content of the distearin by the method of West *et al.* (15) gave the theoretical value.

The distearin was reacted with a mixture of oleoyl and linoleoyl chlorides to give a mixture of oleodistearin and linoleodistearin. The product was crystallized from acetone, giving a 68% yield of material with an iodine value of 42.0 and linoleic acid content of 17.8%. A mixture of only oleodistearin and linoleodistearin containing 17.8% linoleic acid would have an iodine value of 43.8. The mixture of glycerides obtained therefore must have contained about 4% unreacted distearin. This small amount would not be expected to interfere materially with the subsequent fractionations.

Monostearin was prepared, using the isopropylidine group as the blocking agent (16, 17). A 57% yield of recrystallized product was obtained with a melting point of 78.5 to 79°C. X-ray diffraction patterns showed this to be largely the β form of 1-monostearin, for which the reported melting point is 81°C. (14). Determination of the monoglyceride content of the product by the periodate method (18) gave a value of 102%.

TABLE I

Fractional Crystallization Data for a Mixture of Oleodistearin, Linoleodistearin, and Stearodiolein

Fraction	Iodine value	Linoleic acid
		%
Precipitate 1	43.1	11.3
Filtrate 1	57.9	3.0
Precipitate 2	30.9	8.0
Filtrate 2	45.5	12.9
Precipitate 3	40.1	14.1
Filtrate 3	50.4	8.9
Precipitate 4[a]	39.7	12.6
Filtrate 4[a]	54.9	4.9

[a] Crystallized from Skellysolve F.

Monostearin was reacted with oleoyl chloride to give stearodiolein. An 80% yield of recrystallized product was obtained with an iodine value of 56.6 (theoretical 57.2).

Stearodiolein was added to the mixture of oleodistearin and linoleodistearin, and the mixture of the three glycerides was fractionally crystallized from acetone. The fractions remaining after removal of samples for analysis were recombined, and this material was crystallized from Skellysolve F to see if there was any marked difference between a polar and nonpolar solvent. The iodine values and linoleic acid contents of the fractions are given in Table I. The small amount of distearin present in the mixture of disaturated glycerides was concentrated in the least soluble fraction, precipitate 2. As a result, this fraction has a lower iodine value than can be accounted for by any combination of the three glycerides in the mixture having the determined linoleic acid content.

A random mixture of the possible glycerides of stearic, oleic, and linoleic acid was prepared by interesterification of a mixture of the methyl esters of the acids with triacetin, using sodium methoxide as a catalyst. The loss in weight caused by the removal of methyl acetate was 96% of the theoretical. The resulting material had an iodine value of 75.7 and linoleic acid content of 24.6%. This corresponds to a mixture containing 38.6% oleic acid and 36.8% stearic acid.

The random mixture was fractionally crystallized from acetone. The iodine values and linoleic acid contents of the fractions are given in Table II.

TABLE II

Fractional Crystallization Data for Random Mixture of Glycerides

Fraction	Iodine value	Linoleic acid
		%
Precipitate 1	55.6	16.3
Filtrate 1	96.7	31.2
Precipitate 2	88.6	26.3
Filtrate 2	105.2	32.8
Precipitate 3	39.3	11.8
Filtrate 3	72.6	21.9
Precipitate 4	10.0	3.5
Filtrate 4	45.2	13.0

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The Reactions of Hydrogen Bromide with Oleic Acid and Its Esters. II. Free Radical Addition[1]

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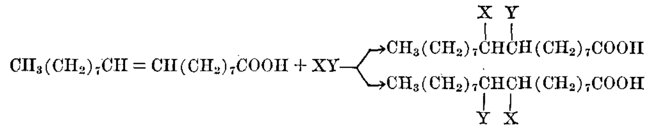
ADDITION of unsymmetrical reagents to the 9,10-double bond of oleic acid can yield a mixture of two-position isomers:



$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH + XY \begin{cases} \rightarrow CH_3(CH_2)_7\overset{X}{C}H\overset{Y}{C}H(CH_2)_7COOH \\ \rightarrow CH_3(CH_2)_7\underset{Y}{C}H\underset{X}{C}H(CH_2)_7COOH \end{cases}$$

In the majority of reactions with unsymmetrical reagents that have been reported the resultant mixtures were not separated. The authors assumed an even distribution at the center since the double bond was too far removed from the carboxyl group to be influenced by means of inductive or other effects. However several reports have appeared in the literature within the last few years where a difference in reactivity at the 9- and 10-carbon atom was observed with derivatives of oleic acid (1, 2, 3). The catalytic hydrogenation of 9,10-epoxystearic acid yielding only 10-hydroxystearic acid was an outstanding example of this type of reaction (4).

In the field of unsaturated fatty acids and their derivatives few investigations have been conducted to study the effect of variations of experimental conditions in addition reactions with hydrogen halides. The formation of chloro-, bromo-, and iodostearic acids by the action of the concentrated inorganic acids on either oleic or elaidic acid were first reported by Piotrowski (5) in 1890. The preparation of fluorostearic acid by the action of hydrogen fluoride in the presence of mercuric chloride was reported more recently (6). The products obtained in all of these reactions were reported as mixtures of the 9- and 10-isomers without regard to the composition of the mixture. After the discovery of the peroxide effect by Kharasch and Mayo (7) some of the simpler fatty acids with terminal double bonds were investigated in hydrogen bromide addition reactions under ionic and free radical conditions (8, 9, 10). However no investigations have been reported on the direction of addition of hydrogen halides to the naturally occurring 18-carbon unsaturated fatty acids.

It was the purpose of our investigation to examine, under closely controlled conditions, one particular addition reaction, namely, the addition of hydrogen bromide to esters of oleic acid. Hydrogen bromide was chosen since it allowed addition under both free radical and ionic conditions. In this paper we are reporting the effects of variations of solvents, dilutions, and temperature on the relative reactivity at the 9- and 10-position of a series of oleate esters when the addition is carried out under free radical conditions.

Experimental

RAW MATERIALS. Pure *methyl oleate* was prepared by the method described by Swern (11). A major portion of the ester was converted to the urea complex for easier preservation (12).

Anal. Calcd. for $C_{19}H_{36}O_2$: S.E., 296; I.V. 85.6. Found: S.E., 295; I.V., 85.8.

Oleic acid was prepared by saponifying methyl oleate with 2 N alcoholic potassium hydroxide for two hours under nitrogen.

Anal. Calcd. for $C_{18}H_{34}O_2$: Neutral Equivalent 382; I.V., 90.0. Found: Neutral Equivalent, 281; I.V., 89.6.

Esters of oleic were prepared, using a Schotten-Baumann procedure by the action of oleoyl chloride on the alcohol which was dissolved in an inert organic solvent containing pyridine as the hydrogen chloride acceptor.

Preparation of Oleoyl Chloride. Oleic acid (84.6 g., .30 mole) was allowed to react with oxallyl chloride (95.1 g., .75 mole) at room temperature and then allowed to reflux one hour. The excess oxallyl chloride was distilled off yielding oleoyl chloride (88.0 g., .29 mole, 98%) which was then distilled, b.p. 185–190°C. at 7–10 mm.; reported b.p. 213°C. at 14.5 mm. (13).

Anal. Calcd. for $C_{18}H_{33}O_{10}$: % free oleic acid, 0.0. Found: % free oleic acid, 0.0 (13a).

Preparation of Phenyl Oleate (14, 15).

Oleoyl chloride (3 g., .01 mole) dissolved in dry ether was added slowly to phenol (0.94 g., .01 mole) and 1.65 ml. pyridine (1.60 g., 0.2 mole). A precipitate was formed and the temperature rose to *ca.* 40°C. The reaction mixture was allowed to stand for half an hour and then was filtered. Water was added and the solution extracted twice with ethyl ether. The ether solution was washed consecutively with water, dilute hydrochloride acid, water, dilute sodium hydroxide and water and then dried over anhydrous sodium sulfate. The solvent was stripped, yielding phenyl oleate (2 g., .0056 mole, 56%) and containing a trace of oleic acid. Saponification equivalent, theoretical 358, found 361.

The material had a slightly yellow color. By dissolving it in ethyl alcohol and removing a small amount of insoluble material, the ester could be recovered as a colorless oil (1.9 g., .00053 mole, 53%). Reported 55% (14).

Anal. Calcd. for $C_{24}H_{33}O_2$: S.E., 357; I.V., 70.9. Found: S.E., 357; I.V., 71.2.

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