Isomerization of Unsaturated Fatty Esters by Iron Pentacarbonyl. Preparation of Iron Tricarbonyl Complexes of Polyunsaturated Fats[1]

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Abstract

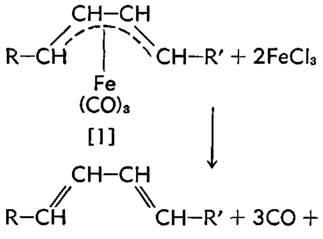
Iron pentacarbonyl is a powerful isomerization agent of unsaturated fatty esters. Highly conjugated fats are obtained when polyunsaturated fatty esters are treated with an excess $Fe(CO)_5$ to form complexes followed by decomposition of the complexes with $FeCl_3$. Iron tricarbonyl complexes were prepared in 80 to 95% yields from methyl linoleate, linolenate and polyunsaturated fatty esters of soybean, linseed and safflower oils by heating at 180–185C with 2 moles $Fe(CO)_5$ per mole ester under nitrogen pressure. Decomposition of these complexes with $FeCl_3$ resulted in 90 to 97% conjugation of the polyunsaturated fatty esters mainly in the all *trans* configuration. Isolated *trans* unsaturation reached levels of 18 to 30%. Methyl oleate yielded 74% *trans* unsaturation but no complex of iron carbonyl was obtained.

Introduction

ARTIFICIALLY CONJUGATED drying oils can be prepared by many different procedures, all aimed at accelerating conjugation of the polyunsaturated fatty acids with a minimum of polymerization. Various aspects of the preparation and properties of artificially conjugated drying oils have been reviewed by Cowan (3) and Bush (1).

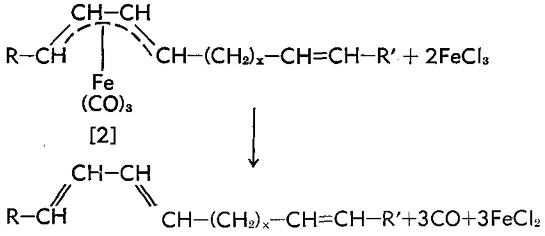
Studies in this Laboratory with homogeneous catalysts for the hydrogenation of unsaturated fats showed that iron pentacarbonyl is a powerful isomerization agent (11), and that it forms stable iron carbonyl complexes with polyunsaturated fatty esters (10). Diene complexes from methyl linoleate were characterized as mixtures of isomeric, conjugated methyl octadecadienoate-iron tricarbonyl (8). Triene complexes from linolenate proved to be mixtures of isomers containing a conjugated diene-$Fe(CO)_3$ unit and a noncomplexed *cis* or *trans* olefinic bond either α,β to the π-complexed system or separated by several methylene groups (7). Hashimoto and Shiina (14) reported the formation of up to 30% conjugated dienes from soybean oil by heating with $Fe(CO)_5$ at 180 and 200C under nitrogen. However they did not consider the formation of iron carbonyl complexes. From methyl linoleate conjuguated with $Fe(CO)_5$ they obtained a mixture of *trans,trans* 9,11- and 10,12-methyl octadecadienoate (15). More recently, Misono et al. (21) and Ogata and Misono (22) reported the formation of iron tricarbonyl complexes from cottonseed oil and dehydrated castor oil methyl esters by hydrogenation or reaction with $Fe(CO)_5$, under nitrogen pressure. This work is in good agreement with ours (8,10) and was published the same year.

Practically, our present studies are aimed at converting soybean, linseed and other vegetable oils into conjugated drying oils, and into new organometallic derivatives by treatment with $Fe(CO)_5$. Theoretically, we are interested in the mechanism of isomerization and conjuguation catalyzed by soluble organometallic complex such as $Fe(CO)_5$. A procedure was developed leading to nearly complete conjugation of polyunsaturated fatty esters or oils by the formation of stable iron tricarbonyl complexes. These complexes can be easily and completely decomposed with ferric chloride to give high yields of conjuguated oils. Decomposition with $FeCl_3$ (24) is formulated below as an oxidation-reduction. The diene-$Fe(CO)_3$ complexes [1] investigated in this work yield *trans,trans* conjugated dienes as follows:

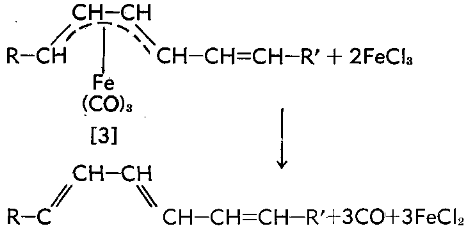


Conjugated dienes

The respective triene-$Fe(CO)_3$ complexes [2] and [3] give conjugated diene-trienes (trienes with a conjugated diene system and an isolated double bond) and conjugated trienes as follows:



Conjugated diene-trienes (x > 1)



Conjugated trienes

Experimental

Materials

The soybean, linseed and safflower oils used were commercially refined. Their methyl esters were obtained by transesterification with potassium methoxide and distillation under vacuum. Methyl oleate and linoleate were obtained from the Hormel Insti-

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[1] Presented in part at AOCS meeting in Houston, 1965.
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tute and analyzed 100% by gas-liquid chromatography (GLC). Methyl linolenate was prepared from linseed esters by counter double current distribution (2), and showed by GLC 98.8% triene and 1.2% diene.

Fractionations and Analyses

Fractionations by countercurrent distribution (CCD), between hexane and acetonitrile, and argentation chromatography on $AgNO_3$-treated cation exchange column were the same as described previously (8,9). The methodology relating to GLC, IR and UV was also the same (9,11). Conjugated dienes (*cis, trans* and *trans,trans*) used as standards for GLC were prepared from alkali-conjugated methyl linoleate. Conjugated diene-trienes and conjugated trienes were prepared from alkali-conjugated linseed oil (11). The iron tricarbonyl complex was determined by IR in the carbonyl stretching region (4–6 μ) in CCl_4 solutions. Pure methyl octadecadienoate-$Fe(CO)_3$ derived from methyl linoleate (8) was used as standard. Its respective absorptivity at 4.88 and 5.05 μ was 4.54 and 7.95 and followed Beer-Lambert's Law in the range of 10 to 100% complex. Double bond location in fractionated fatty esters was determined by the $KMnO_4$-KIO_4 cleavage technique of Jones and Davison (17).

Preparation of $Fe(CO)_3$ Complex

All complex preparations were made in a 150-ml or 300-ml magnetically stirred Magne-Dash, high-pressure autoclave adapted with sampling tube and cooling coil. All operations with $Fe(CO)_5$ were carried out in a well-ventilated hood and without exposure to direct light. In a typical run (run 4, Table I) 30.22 g of soybean oil methyl esters (0.1 mole) was charged into a 150-ml autoclave together with 28 ml (39.2 g, 0.2 moles) of $Fe(CO)_5$. The mixture was deaerated by gentle nitrogen bubbling. The sealed autoclave was then purged three times with nitrogen at a pressure of 100–125 psi with stirring. After releasing the pressure, the autoclave was again charged with 50 psi nitrogen before heating. Complete removal of air at this point was essential to prevent subsequent polymerization of the unsaturated fatty esters and decomposition of $Fe(CO)_5$. The reaction mixture was heated to 185C. The pressure in the system reached a maximum of 195 psi after a 0.5-hr reaction and then decreased to 130 psi after 2 hr when the reaction was complete. The reaction was followed by sequential analyses by GLC and was stopped when the nonconjugated polyunsaturated fatty esters reached a constant value. At this point the autoclave was cooled to room temperature. The reaction mixture was transferred with petroleum ether (bp 39–52C) into a round-bottom flask. Unreacted $Fe(CO)_5$ and other higher boiling unidentified species of iron carbonyls were removed by evacuation in an all-glass rotating evaporator at 25 to 60C with a water aspirator and then 60 to 80C with a vacuum pump (2–3 mm Hg) equipped with a dry ice trap. The dark oil was redissolved in petroleum ether and treated repeatedly with dilute HCl (2:1) until the washings were clear. The yellow oil solution was then washed with water to neutrality and dried over Na_2SO_4. After removal of solvent, the complexed product (35.64 g) was clear and deep yellow or orange. In another run (run 18, Table I) 60.25 g linseed oil and 56 ml $Fe(CO)_5$ were reacted in a 300-ml autoclave at 185C for 2 hr as above, and 76.25 g of complexed oil was obtained.

TABLE I

Iron Tricarbonyl Complex Formation with Unsaturated Fats

Run No.	Samples	$Fe(CO)_5$, M/M	Temperature, C	Time, hr	Complex,[a] %	Yield,[b] %
			Methyl Esters			
1	Soybean	0.5	180	4.5	35.2	53.4
2	Soybean	1.0	180	4	37.9	57.8
3	Soybean	2.0	180	4	43.8	66.5
4	Soybean	2.0	185	2	59.0	89.5
5	Linseed	0.5	180	6	37.0	52.0
6	Linseed	2.0	180	6	48.3	67.8
7	Linseed	2.0	185	2	65.8	92.4
8	Safflower	2.0	175	1 × 5[c]	65.5	79.2
9	Safflower	2.0	180	2.5	76.5	92.5
10	Oleate	1.5	180	5	0	0
11	Linoleate	1.1	180	3	68.2	68.2
12	Linoleate	2.0	180	4	89.8	89.8
13	Linolenate	1.1	180	4	69.0	69.0
14	Linolenate	2.0	180	2 × 2[c]	78.3	78.3
			Triglycerides			
15	Soybean	2.0	180	2 × 2[c]	50.8	77.2
16	Soybean	2.0	185	2	55.7	84.6
17	Linseed	2.0	180	2 × 4[c]	59.6	83.7
18	Linseed	2.0	185	2	67.6	95.0
19	Safflower	2.0	180	2 × 5[c]	67.9	82.1
20	Safflower	2.0	185	4	75.4	91.2

[a] Expressed as methyl octadecadienoate-$Fe(CO)_3$.

[b] Based on mole % polyunsaturated fatty esters in original samples; calculated yields of complex: soybean, 65.9%; linseed, 71.2%, and safflower, 82.7%.

[c] Interrupted runs. Example, Run 8: react 1 hr, cool to room temperature, recharge with N_2, reheat and repeat five times.

Decomposition of Complex

Complexed soybean oil esters (10.05 g, run 4, Table I) were dissolved in 95% EtOH in an Erlenmeyer flask, and the mixture was stirred magnetically with nitrogen bubbling. Small portions of $FeCl_3 \cdot 6H_2O$ were added to the solution until no more CO was evolved (30 g $FeCl_3$ used). Stirring was continued under nitrogen for 1 hr. The mixture was then diluted with water and extracted three times with petroleum ether. The washed extract was dried (Na_2SO_4), and the solvent removed to give 7.90 g conjugated esters.

Complexed triglycerides were decomposed by a similar procedure as the methyl esters except that they were dissolved in a mixture of benzene and 95% EtOH and that more $FeCl_3$ was used. In a typical example (run 18, Table I) 12.02 g of complexed linseed oil was dissolved in a mixture of 200 ml benzene and 350 ml 95% EtOH. The solution was stirred with nitrogen bubbling and 60 g $FeCl_3$ was added in small portions. Stirring was continued 2 hr under nitrogen. The conjugated oil (9.40 g) was isolated as above.

Results

The effect of reaction conditions on yields of iron tricarbonyl complex was studied. The results in Table I show that the yield of complex increased with initial concentration of $Fe(CO)_5$ at 180C. Moreover, the reaction proceeded much more smoothly at 180C and 185C than at 175C, giving 90 to 92% yields of complex. Temperatures higher than 185C would be expected to result in polymerization of the conjugated esters (21).

With methyl oleate no stable complex was formed by reaction with $Fe(CO)_5$, but extensive positional and geometric isomerization of the double bond occurred. With methyl linoleate it was necessary to use 2 moles $Fe(CO)_5$ per mole ester to obtain 90% conversion to complex at 180C. With methyl linolenate a yield of 78% complex was obtained by heating 2 hr with 2 moles $Fe(CO)_5$, cooling to room temperature, releasing the CO formed and reheating for another 2 hr. With triglycerides the yield of complex obtained ranged from 85 to 95%.

The iron carbonyl-complexed fats were completely decomposed with $FeCl_3$, as evidenced by the disappearance of the bands at 4.88 and 5.05 μ which are due to carbonyl stretching. Composition of the conjugated products obtained after decomposition of complex is summarized in Table II. Analyses by GLC and IR show that the conjugated dienes and trienes are predominantly in the all-*trans* configuration. The UV analyses for conjugated dienes approximate those of GLC if an absorptivity at 230 mμ of 100 is used. Methyl linolenate and the linseed esters contained mixtures of conjugated dienes, conjugated diene-trienes and conjugated trienes. UV analyses show also high diene and triene conjugation in isomerized linolenate. Agreement between the analyses of distilled and nondistilled isomerized esters (runs 7 and 8, Table II) and between GLC and UV for conjugated dienes shows that little or no polymerization occurred during the reaction with $Fe(CO)_5$. Therefore, it is concluded that the degree of conjugation exceeds 90% in the products obtained by reaction of the polyunsaturated fatty esters with $Fe(CO)_5$.

Isolated *trans* unsaturation measured by IR in the isomerized fatty esters ranged from 18 to 30%. In pure methyl oelate isomerized with $Fe(CO)_5$, the *trans* unsaturation reached 65% (run 10, Table II). Taking into account the nonmonoene components, a calculated value of 74.2% *trans* is obtained. In isomerized methyl linolenate, the isolated *trans* unsaturation must be due to the isolated double bond of the conjugated diene-trienes. The small amount of stearate and diene determined in oleate indicates that the isomerization by $Fe(CO)_5$ was accompanied by a little hydrogenation and a corresponding amount of dehydrogenation. Smaller amounts of hydrogenation are also evident in linoleate and linolenate isomerized with $Fe(CO)_5$ (runs 12 and 14, Table II).

A more detailed analysis of isomers was obtained in $Fe(CO)_5$-treated fatty esters by CCD fractionation between hexane and acetonitrile. Figure 1 shows the separation of $Fe(CO)_5$-treated soybean esters into four peaks. The shaded area under peaks III and IV indicates the presence of iron carbonyl complexes by $AgNO_3$-TLC. The same CCD fractionation was carried out on $Fe(CO)_5$-treated methyl linoleate and linolenate. Analyses of the CCD fractions are given in Table III. The monoene (fraction I) shows high proportions of *trans* unsaturation. The dienes (fraction II) are mixtures of unconjugated isomers with high isolated *trans* unsaturation and of conjugated isomers in the *cis,trans* and *trans,trans* configuration. The iron carbonyl complexes were separated into diene-$Fe(CO)_3$ (fraction III) and triene-$Fe(CO)_3$ (fraction IV). Fraction III includes also noncomplexed trienes which, in linolenate, consist of a mixture of conjugated diene-trienes and conjugated trienes predominantly in the all-*trans* configuration. Pure diene-$Fe(CO)_3$ complex was obtained from methyl linoleate (fraction III). The triene-$Fe(CO)_3$ complex was 92% pure in fraction IV of methyl linolenate. Decomposition of the diene complex with $FeCl_3$ yielded pure conjugated diene, 90 to 95% in the *trans,trans*-configuration (GLC). Decomposition of the triene complex gave a mixture of conjugated diene-trienes (46%) and conjuguated trienes (54%) in the all-*trans* configuration.

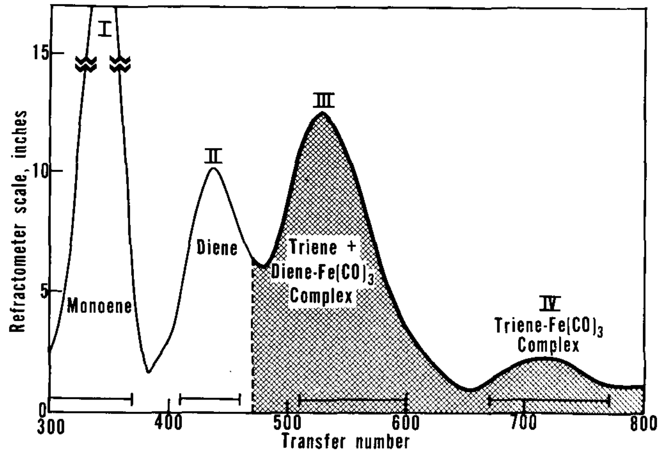

FIG. 1. Countercurrent distribution of soybean oil methyl esters treated with $Fe(CO)_5$ (run I, Table III) between hexane and acetonitrile in a 200-tube instrument.

The distribution of double bonds in fractions from $Fe(CO)_5$-treated soybean esters is given in Figure 2. The conjuguated dienes derived from decomposed diene-$Fe(CO)_3$ complex (fraction III, Fig. 1) show that the 9–11 and 10–12 dienes comprise 67% of the

TABLE II

Fatty Acid Composition of Fats Conjugated with Iron Pentacarbonyl[a]

Analyses	Soybean Esters		Linseed Esters		Safflower Esters			Oleate Run 10	Lino-leate Run 12	Lino-lenate Run 14	Soybean Oil Run 15	Linseed Oil Run 18	Saf-flower Oil Run 20
	Run 3	Run 4	Run 7	Run 7[b]	Run 8	Run 8[b]	Run 9						
Gas-liquid Chromatography, %													
Palmitate	11.4	9.9	6.8	6.3	6.2	5.6	4.9	....	....	....	11.4	7.5	7.3
Stearate	4.2	3.7	4.8	4.1	2.4	2.7	3.2	6.0	....	....	4.1	4.8	2.3
Monoene	28.2	29.8	24.9	23.3	18.3	19.8	19.1	88.0	0.5	....	28.7	26.2	14.6
Diene[c]	7.4	1.8	1.6	3.5	4.1	3.0	0.9	6.0	2.3	1.6	1.0	1.3	1.5
Conjugated diene													
cis,trans[d]	11.1	6.8	2.6	3.6	8.9	6.9	4.2	....	9.8	....	4.3	2.4	3.3
trans,trans	37.7	48.0	....	....	60.0	62.0	66.7	....	87.4	3.3	43.4	20.0	71.0
Conjugated diene-triene[e]	....	....	36.1	36.1	....	....	....	....	....	40.5	4.2	15.0	....
Conjugated triene	....	....	23.2	23.1	....	....	....	....	....	54.6	2.9	22.8	....
Conjugation[f]	86.0	96.6	94.7	94.5	90.0	90.0	92.6	....	97.2	98.4	96.6	95.8	97.2
Infrared													
[a]10.1 μ	0.478	0.550	0.485	0.570	0.717	0.726	0.842	....	1.065	0.807	0.574	0.561	0.841
[a]10.6 μ	0.026	0.019	....	....	....	....	....	....	....	....	....	....	....
Isolated *trans*,[g] %	18.2	23.4	26.0	29.9	20.6	19.6	20.2	65.3(74.2)[h]	....	22.4	21.8	25.8	17.5
Ultraviolet													
[a]231 mμ	45.8	52.6	37.0	38.1	73.7	69.7	72.7	....	99.5	40.8	51.2	35.5	75.97
[a]268 mμ	6.46	6.86	51.4	54.1	....	....	....	....	....	85.4	68.0	50.2	....

[a] Same runs as in Table I analyzed after decomposition of iron carbonyl complexes with ferric chloride.
[b] Distilled at 145C/0.02 mm Hg, recovery 95%.
[c] Partially resolved into 3 component peaks.
[d] Includes triene when not completely conjugated.
[e] In linseed esters the conjugated diene-triene are not well separated from *trans,trans* conjugated dienes and are summed together.
[f] Based on total linoleate and linolenate in original samples: soybean, 56.7; linseed, 62.6; and safflower, 76.5%.
[g] Expressed as methyl elaidate.
[h] Adjusted value to take into account nonmonoene component.

TABLE III

Analyses of Countercurrent Distribution Fractions from $Fe(CO)_5$-Treated Fatty Esters [a]

Analyses	Fractions						
	I	II		III			IV
	Soybean	Soybean	Linoleate	Soybean [b]	Linoleate [b]	Linolenate	Linolenate [b]
Countercurrent distribution, %	40.1	22.7	36.5	32.0[c]	63.5[c]	37.3	62.7[c]
Gas-liquid chromatography, %							
Monoene (saturates)	63.8 (32.8)	.....	......	......	......	......	......
Diene	3.6	23.0	45.4	......	......	......	......
Conjugated diene							
cis,trans	......	44.5	25.5	8.0	4.7	......	......
trans,trans	......	32.5	29.1	89.4	95.3	.....	......
Conjugated diene-triene	......	......	......	2.6	......	60.6	45.8
Conjugated triene	......	......	......	......	......	39.4	54.2
Infrared							
[a]10.1 μ	......	0.44	0.39	1.04	1.26	0.46	0.64
[a]10.6 μ	......	0.13	0.08	......	......	0.03	......
Isolated *trans*,[d] %	32.2 (51.4)[e]	23.8	62.9	......	......	31.4	33.4
Ultraviolet							
[a]230 mμ	......	68.0	54.4	86.8	105.2	42.8	31.3
[a]267 mμ	......					53.1	31.1

[a] Soybean, run 1; linoleate, run 11; linolenate, run 13 (see Table I).
[b] Analyzed after decomposition of complex with ferric chloride.
[c] Before decomposition of complex with ferric chloride.
[d] Expressed as methyl elaidate .
[e] Adjusted value includes nonmonoene components.

total, the remainder consisting of the 6–8, 7–9, 8–10, 11–13 and 12–14 isomers. The monoene fraction shows scattering of the double bond between the 4 and 16 positions with only 27% remaining in the original 9 position. Methyl oleate isomerized with $Fe(CO)_5$ (run 10, Table I) was separated into the *cis* (26%) and *trans* (74%) isomers by argentation column chromatography. The relative concentration of these isomers is in agreement with the *trans* content determined by IR (Table II, adjusted value), and corresponds to the equilibrium composition reported by Litchfield et al. (18) in oleate isomerized with selenium and nitrous acid. The double bond in these isomers is also distributed between the 4 and 16 positions (Fig. 3). The proportion of the double bond remaining in the original 9 position is 12 and 11% in the *cis* and *trans* fractions, respectively.

Discussion

This study has shown that considerable geometric and positional isomerization occurs when unsaturated fats are heated with $Fe(CO)_5$. A process has been developed to conjugate 90 to 98% of the polyunsaturated fatty acids in vegetable oils. This new method is based on complexing the polyunsaturated fatty esters with iron carbonyl and then decomposing the complexes with $FeCl_3$. The iron carbonyl-complexed oils obtained in yields of 80 to 95% are new organometallic derivatives, which may be useful either as organic intermediates or as coating materials. Similar complexes have found uses as catalysts for olefin, polymerization and as fuel additives (13). The *trans, trans* configuration of the conjugated dienes should make them particularly suitable for Diels-Alder addition reactions (5,16,27) and for dimerization (4). Both the complexed and the conjugated oils are now being evaluated in this Laboratory as coating materials. New ways to decompose the iron carbonyl-complexed oils are also being investigated in an attempt to recover free iron carbonyl for reuse. Such a procedure would make this new process for the conjugation of fats more economical and competitive with other methods used in industry to convert vegetable oils into conjugated drying oils (1,3).

Several reports in the literature have described the isomerization of olefins with metal carbonyls and the mediation of metal carbonyl π-olefin complexes has been postulated (20,23,26). The diene and triene-$Fe(CO)_3$ π-complexes of linoleate and linolenate could serve as good model systems for the isomerization of unsaturated fats by soluble and insoluble catalysts. The formation of catalyst addition products has been observed during the isomerization of oleic acid by "NO_3" (12) and by selenium (6). Evidence was ob-

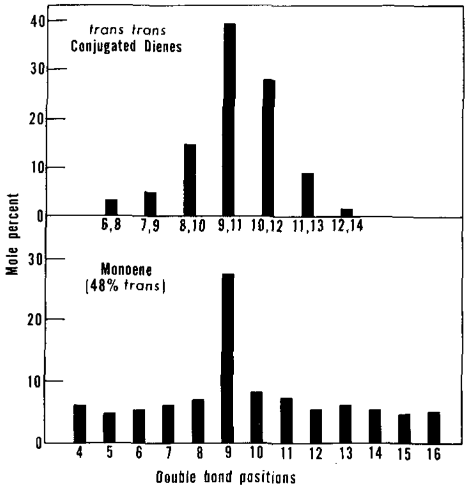

FIG. 2. Double bond distribution in fractions from soybean oil methyl esters treated with $Fe(CO)_5$. Top: *trans,trans*-conjugated dienes (decomposed fraction III, run 1, Table IV); bottom: monoene (fraction I, run I, Table III).

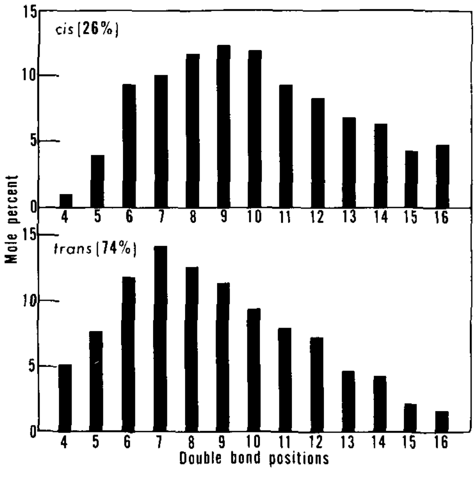

FIG. 3. Double bond distribution of *cis* and *trans* monoenes from methyl oleate isomerized with $Fe(CO)_5$ (run 10, Table I).

tained for π-complex formation between oleic acid and selenium (6). The possibility of π-complex formation between NO_2 and an olefinic bond was also suggested in the elaidinization of ricinoleic acid (19). Moreover, in the heterogeneous catalysis by metals, π-complexed intermediates were postulated (25). All these complexes are probably related to the iron tricarbonyl complexes of unsaturated fats which are easier to purify and characterize.

ACKNOWLEDGMENT

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