Competitive Hydrogenation Rates of Isomeric Methyl Octadecadienoates

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ABSTRACT

Determination of the relative reaction rates of isomeric methyl octadecadienoates is possible by competitive reduction of a mixture containing an inactive diene and a radioactively labeled isomer. The hydrogenation rate of methyl *cis*-9,*cis*-12-octadecadienoate with platinum and nickel catalysts is compared to the hydrogenation rate of each of several isomers of methyl octadecadienoate, and the relative rate of the competitive hydrogenations is calculated by a digital computer. Methyl *cis*-9,*cis*-12 linoleate is reduced the most rapidly of all the dienes studied. The relative rates of the positional isomers tend to decrease with the increasing number of methylene groups between the double bonds, except when one of the double bonds is in the more reactive 15 position. Comparison of the geometric isomers shows that *trans,trans* diene is hydrogenated at a slower rate than *cis,cis* linoleate.

INTRODUCTION

It generally is recognized that hydrogenation rates differ with structure of fatty acid isomers. A summary of earlier work and our own results on methyl octadecenoates appear in a previous paper (1). Fewer data are available on comparison of hydrogenation rates of polyunsaturated esters, although the comparison between polyunsaturates and monounsaturates has been considered widely in terms of the selectivity so important in commercial hardening of edible oils. In one of the few comparisons of octadecadienoate esters, Bailey (2) showed that "isolinoleate" formed from linolenate during hydrogenation was reduced much more slowly than natural linoleate; and Hilditch (3) suggested that the great difference in hydrogenation rates between naturally occurring *cis*-9,*cis*-12-linoleate and isolinoleate or monounsaturates was caused by the greater reactivity of the methylene group between the 9- and 12-double bonds.

Isomeric octadecadienoates are formed during hydrogenation and their products upon reduction have been studied (4-6). A knowledge of their reduction rates relative to those of other fatty acids in an oil will increase our understanding of hydrogenation reactions in the oil. In this paper, we compare competitive reduction rates of a number of positional and geometric octadecadienoic esters with methyl *cis*-9,*cis*-12-linoleate using techniques and methods of calculation similar to those used in an earlier paper on octadecenoates (1).

EXPERIMENTAL PROCEDURES

Methyl *cis*-9,*cis*-12-octadecadienoate was isolated from safflower methyl esters by counter double current distribution (7). Methyl *trans*-9,*trans*-12-octadecadienoate was prepared by treating methyl linoleate with nitrous oxide as described by Harlow, et al., (8) and the *trans,trans* diene was isolated by argentation countercurrent distribution (9). Methyl *cis*-9,*cis*-15-linoleate was prepared by argentation countercurrent distribution of dienes from hydrazine-reduced linolenic acid (10). Methyl *cis*-9,*trans*-12-linoleate was prepared in the laboratory by dehydration of ricinoleic acid and isolated by argentation countercurrent distribution (10). The *cis,cis*-5,12-; -6,10-; -6,11-; -6,12-; -7,12-; and -8,12-methyl octadecadienoates are synthetic products furnished by F.D. Gunstone.

Methyl *cis*-9,*cis*-12-linoleate-1-^{14}C was prepared from linoleic acid-1-^{14}C (11) purchased from Amersham-Searle, Des Plaines, Ill. Methyl esters with the methoxyl group labeled with tritium were prepared according to Mounts and Dutton (12).

The catalysts were 5% platinum on carbon purchased from Baker and Co., Phillipsburg, N.J. and Girdler G-15 nickel in hardened cottonseed oil obtained from Chemetron Corp., Louisville, Ky.

Methyl esters were reduced in the precision hydrogenator described by Rohwedder (13) modified with a glass reaction flask so that samples could be removed during hydrogenation. All hydrogenations were run at one atmosphere pressure. At 50 C, platinum-on-carbon catalyst with ca. 0.1% platinum metal was used; G-15 nickel catalyst with ca. 0.2% nickel was used with the temperature at 140 C. The hydrogenation vessel, with the weighed catalyst, was evacuated, flushed, and filled with hydrogen. The vessel was heated in a constant temperature oil bath. After the system was at reaction temperature, a 300 mg methyl ester sample containing a radioactive tracer was injected into a sidearm fitted with a rubber septum. Hydrogen uptake was monitored by a strip chart recorder (13); zero time is when agitation begins. Eight samples, each ca. 20 μliter, were removed for analysis.

For single-labeled experiments a sample consisted of one unlabeled diene with a trace amount of a radioactive diene isomer so that the specific activity of the whole mixture was 1 μc/mg. For dual-labeled experiments, methyl *cis*-9,*cis*-12-linoleate-1-^{14}C and a tritiated isomer were blended with the inactive mixture of these two esters.

Since hydrogenation behavior of dienes with widely separated double bonds tends to resemble that of monoenes (2,3), relative hydrogenation rates are expected to vary greatly with conditions of hydrogenation much as selectivity of dienes over monoenes has been found to vary. We have attempted to characterize our catalysts and hydrogenation conditions by determining selectivity ratios (R_{Lo}/R_{Ol}) by Albright's procedure (14) as suggested by the AOCS Hydrogenated Oil Subcommittee (15). Selectivity ratio of nickel is 15 and of platinum, 2.

Analysis

Partially hydrogenated samples containing one radioactive isomer were analyzed with a Cary-Loenco instrument (16) in which the unlabeled esters are detected by thermal conductivity, and the radioactive esters are monitored by a spherical ion chamber. Data were stored with a two-channel magnetic tape recorder and played back to an IBM 1800 computer programed to integrate the curves and calculate composition of inactive and radioactive esters.

Dual-labeled samples were analyzed on an Aerograph model A-90P gas chromatograph modified to provide for serial collection of the gas chromatographic column effluent in scintillation solvent (17). The radiochemical fractions collected were counted in a Beckman LS-250 liquid scintillation counter hardware wired to an IBM 1800 computer

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programed to calculate the disintegrations/min of the ^{14}C and ^{3}H isotopes and the composition of ^{14}C and ^{3}H esters.

RESULTS AND DISCUSSION

The hydrogenation rate of each isomer has been compared with that of methyl *cis*-9,*cis*-12-linoleate assuming the reaction model:

$$\begin{tikzcd} \text{Diene } c9,c12 \arrow[r, "k_1"'] \arrow[rr, bend left, "k_3"] & \text{Monoene} \arrow[r, "k_2"'] & \text{Stearate} \end{tikzcd}$$

$$\begin{tikzcd} \text{Diene A} \arrow[r, "k_4"'] \arrow[rr, bend left, "k_6"] & \text{Monoene} \arrow[r, "k_5"'] & \text{Stearate} \end{tikzcd}$$

Then the hydrogenation rate of diene A relative to methyl *cis*-9,*cis*-12-linoleate is $(k_4 + k_6)/(k_1 + k_3)$—the total rate of disappearance of diene A compared to linoleate. Values for the constants which are calculated as described by Butterfield (18) are under column A of the tables. In these calculations, the experimental compositions of esters from both substrates are plotted against the remaining double bonds in products from the methyl *cis*-9,*cis*-12-linoleate. A typical plot of these calculations is shown in Figure 1. Composition of the products from diene A is plotted against the same X coordinate. Rate constants are determined by digital computer to give the best fit of curves to experimental points. In most hydrogenations, shunts—$k_3/(k_1 + k_3)$ and $k_6/(k_4 + k_6)$—of 20-30% were found with platinum but not with nickel. This finding is in agreement with our previous work (19). An exception was the 9,15 linoleate, where a shunt, $k_6/(k_4 + k_6)$, of ca. 25% was found with nickel but no shunt, $k_3/(k_1 + k_3)$, occurred for the 9,12 linoleate in the same reaction vessel with it. Hooper (20) has suggested a simpler calculation using a linear regression formula and values calculated by his method appear under column B of the tables. Values calculated by the two methods agree, except for positional isomers with nickel, where the trend is observed that the Hooper calculation gives higher values. Values given in column A and column B in the tables are averages of two separate hydrogenations.

A statistical analysis of the data shows that, for positional isomers, the least significant difference between samples in column A is 0.056 and in column B, 0.125 (Table I). For *cis,trans* isomers, the least significant difference in column A is 0.094 and in column B, 0.125 (Table II).

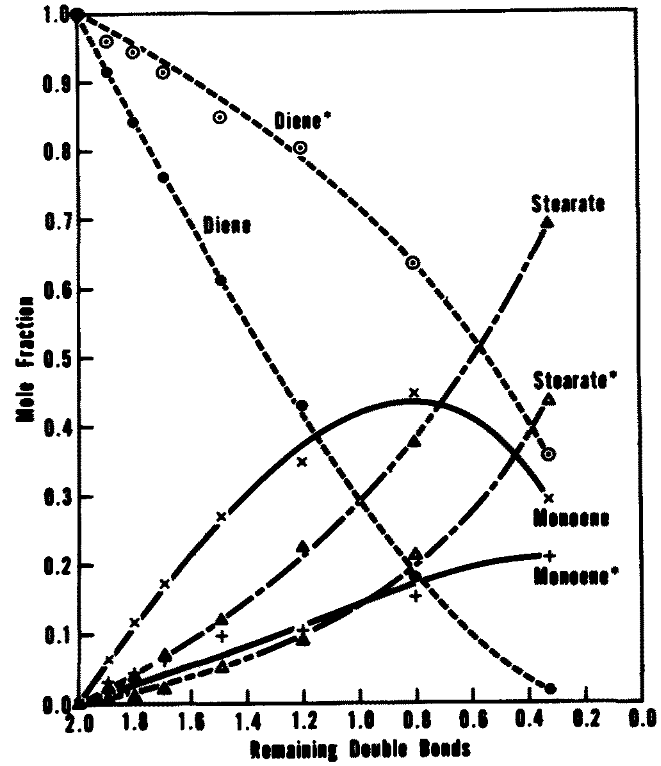

FIG. 1. Hydrogenation of a mixture of *cis*-9,*cis*-12 linoleate and **cis*-6,*cis*-12 isomer with Pt catalyst. Calculation of relative reaction rates. Asterisk denotes radioactive esters. X-axis refers to products from methyl *cis*-9,*cis*-12-linoleate.

The great difference in hydrogenation rates between fatty acids having one methylene group or more than one between the double bonds was pointed out by Hilditch (3). From our experimental work, we have found this difference to be equally true with most of the positional isomers. *cis*-9,*cis*-12-Octadecadienoate with one methylene group between the two double bonds is reduced the most rapidly. Increasing the number of methylene groups between the double bonds increases the difference in rates between *cis*-9,*cis*-12-linoleate and its positional isomers. The *cis*-9,*cis*-15-diene is reduced more rapidly than would be expected for four methylene groups between the double bonds. However, the *cis*-15 monoene reportedly is also more reactive with hydrogen (1) than monoenes that have double bonds closer to the center of the chain.

With nickel, the hydrogenation rate of the positional isomers compared to the *cis*-9,*cis*-12 ester decreased more than with platinum. This decrease is in agreement with the greater selectivity of nickel than of platinum for linoleate

TABLE I

Competitive Hydrogenation Rates of Positional Isomers of Methyl Octadecadienoate[a]

		$k/k_{c9,c12}$[b]			
		Pt		Ni	
Mixture of *cis*-9,*cis*-12 (ca. 100%) with ^{3}H labeled isomers (trace)	No. of $-CH_2-$ groups between double bonds of labeled isomer	A[c]	B[d]	A[c]	B[d]
cis-6,*cis*-10	2	0.488	0.470	0.118	0.165
cis-8,*cis*-12	2	0.430	0.430	0.120	0.305
cis-6,*cis*-11	3	0.302	0.210	0.082	0.100
cis-7,*cis*-12	3	0.370	0.355	0.072	0.220
cis-6,*cis*-12	4	0.262	0.265	0.045	0.080
cis-9,*cis*-15	4	0.540	0.540	0.152	0.330
cis-5,*cis*-12	5	0.322	0.365	0.040	0.070

[a] Column A = relative rates calculated by computer program (18). Column B = relative rates calculated by linear regression formula (20).

[b] Reaction rate of isomer divided by rate of methyl *cis*-9,*cis*-12-octadecadienoate.

[c] Least significant difference between samples is 0.056.

[d] Least significant difference between samples is 0.125.

TABLE II

Competitive Hydrogenation Rates of Geometric Isomers of Methyl Octadecadienoate[a]

Mixture of *cis*-9,*cis*-12 (ca. 100%) with ^{3}H labeled isomers (trace)	$k/k_{c9,c12}$[b] Pt A[c]	Pt B[d]	Ni A[c]	Ni B[d]
cis-9,*trans*-12	0.762	0.595	0.748	0.785
trans-9,*trans*-12	0.712	0.750	0.638	0.660
cis-9,*cis*-15	0.540	0.540	0.152	0.330
trans-9,*trans*-15	0.362	0.295	0.102	0.110

[a]Column A = relative rates calculated by computer program (18). Column B = relative rates calculated by linear regression formula (20).

[b]Reaction rate of isomer divided by rate of methyl *cis*-9,*cis*-12-octadecadienoate.

[c]Least significant difference between samples is 0.094.

[d]Least significant difference between samples is 0.125.

TABLE III

Effect of Composition upon Relative Hydrogenation Rates[a]

Mixture		$k/k_{c9,c12}$[b] Pt A	Pt B	Ni A	Ni B
cis-9,*cis*-12 ^{3}H *trans*-9,*trans*-12	ca. 100% Trace	0.712	0.750	0.638	0.660
^{14}C *cis*-9,*cis*-12 3H *trans*-9,*trans*-12	50% 50%	0.442	0.400	0.615	0.655
14C *cis*-9,*cis*-12 ^{3}H *trans*-9,*trans*-12	25% 75%	c	c	0.518	0.555
^{3}H *cis*-9,*cis*-12 *trans*-9,*trans*-12	Trace ca. 100%	0.290	0.175	0.480	0.405
cis-9,*cis*-12 ^{3}H *cis*-9,*cis*-15	ca. 100% Trace	0.540	0.540	0.152	0.330
^{14}C *cis*-9,*cis*-12 ^{3}H *cis*-9,*cis*-15	50% 50%	0.555	0.560	0.165	0.305
^{3}H *cis*-9,*cis*-12 *cis*-9,*cis*-15	Trace ca. 100%	0.200	0.140	0.058	0.060

[a]Column A = relative rates calculated by computer program (18). Column B = relative rates calculated by linear regression formula (20).

[b]Reaction rate of isomer divided by rate of methyl *cis*-9,*cis*-12-octadecadienoate.

[c]Only run with nickel catalyst.

over monoenes; it is related to the proportion of linoleate that is reduced through a conjugated intermediate. Scholfield (4) found, in hydrogenations under similar conditions, that 15% *cis*-9,*cis*-12-linoleate is reduced through a conjugated intermediate with platinum and 54% with nickel; with more than one methylene group between the double bonds, conjugation does not occur so readily. Therefore, the overall relative rate decreases more when nickel is the catalyst. As can be seen from Table I, with nickel catalyst, the difference of relative rates between isomers is small. There is no significant difference between isomers when the two double bonds are the same distance apart. With platinum, many differences are significant, even among isomers that have the same number of methylene groups between the double bonds.

The geometric diene isomers containing *trans* double bonds generally are reduced more slowly in the same way that monoenes are when nickel is the catalyst (1). Previous work has shown that the *cis* monoenes reduce faster than *trans* monoenes. Both the 9,12 and 9,15 series of isomers react in this way. In Table II, with nickel, *cis*-9,*trans*-12-linoleate is more reactive than the *trans*-9,*trans*-12 isomer; however, with platinum, the relative rates are not significantly different.

If the model upon which these calculations are based is completely valid, similar rates, differing only because of experimental variation, should result whether the calculations are based upon the remaining double bonds in the radioactive ester (the trace minor component) or the inactive ester (the major component). This premise has been found to be true. Also, similar rates should result when the radioactive label is placed on methyl *cis*-9,*cis*-12 linoleate and the other ester is the major component. However, the relative rate differs for the mixtures of *cis*-9,*cis*-12 with either the *trans*-9,*trans*-12 or *cis*-9,*cis*-15 isomers. Similar tests were not run with other positional esters because of limited material.

Because relative rates did vary with the mass composition of the mixture, dual-labeled hydrogenations were run in which the amounts of each isomer were varied (Table III). When present in small amounts, the isomeric ester hydrogenates faster relative to *cis*-9,*cis*-12-linoleate than when it is present in larger amounts. With the *cis*-9,*cis*-15 ester for both catalysts and with the *trans*-9,*trans*-12 ester for nickel, the relative rate is higher at least in a 50% mixture. With *trans*-9,*trans*-12-linoleate and platinum, the change is more nearly linear with a change in composition (Fig. 2).

This effect of composition upon reduction rates is not adequately explained; it may be related to competitive adsorption of the two isomers at the catalyst surface, but there seems to be no satisfactory experimental way to separate adsorption effects from rate of hydrogen transfer to the adsorbed molecule.

By running the hydrogenations and comparing the *cis*-9,*cis*-12 diene to *trans*-9,*trans*-12-linoleate and to *cis*-9,*cis*-15-linoleate, consecutively by the technique discussed by Hussey, et al., (21) we found that relative rates (Table IV) are higher than when hydrogenations are run competitively at the same time.

These competitive inhibitive effects are of interest in studies of the hydrogenation mechanism, but since *cis*-9,*cis*-12-linoleate is the diene naturally present in vegetable oils, and since it remains in large amounts compared to other dienes during most of the hydrogenation, the higher values for relative rates of *cis*-9,*cis*-12-linoleate correspond to the composition found in such systems.

ACKNOWLEDGMENTS

The synthetic isomers were furnished by F.D. Gunstone, St. Salvator's College, The University, St. Andrews, Scotland. W.F. Kwolek, biometrician, stationed at the Northern Laboratory, did the statistical analyses.

REFERENCES

1. Scholfield, C.R., T.L. Mounts, R.O. Butterfield, and H.J. Dutton, JAOCS 48:237 (1971).
2. Bailey, A.E., Ibid. 26:644 (1949).
3. Hilditch, T.P., J. Oil Colour Chem. 30:1 (1947).
4. Scholfield, C.R., JAOCS 49:583 (1972).
5. Koritala, S., C.R. Scholfield, E. Selke, and H.J. Dutton, Ibid. 50:11 (1973).
6. Koritala, S., and H.J. Dutton, Ibid. 50:307 (1973).
7. Scholfield, C.R., R.O. Butterfield, and H.J. Dutton, Lipids 1:163 (1965).
8. Harlow, R.D., C. Litchfield, and R. Reiser, JAOCS 40:505 (1963).
9. Scholfield, C.R., E.P. Jones, R.O. Butterfield, and H.J. Dutton, Anal. Chem. 35:1588 (1963).
10. Butterfield, R.O., C.R. Scholfield, and H.J. Dutton, JAOCS 41:397 (1964).
11. Metcalf, L.D., and A.A. Samitz, Anal. Chem. 33:363 (1961).
12. Mounts, T.L., and H.J. Dutton, J. Label. Compounds 3:343 (1967).
13. Rohwedder, W.K., J. Catal. 10:47 (1968).
14. Albright, L.F., JAOCS 42:250 (1965).
15. AOCS Hydrogenated Oil Subcommittee, JAOCS 50:334A (1973).
16. Nelson, D.C., P.C. Rissler, and R.C. Howe, Anal. Chem. 35:1575 (1963).
17. Thomas, P.J., and H.J. Dutton, Ibid. 41:657 (1969).
18. Butterfield, R.O., JAOCS 46:429 (1969).
19. Scholfield, C.R., R.O. Butterfield, and H.J. Dutton, Ibid. 49:586 (1972).
20. Hooper, D.L., Ibid. 49:446 (1972).
21. Hussey, A.S., G.W. Keulks, G.P. Nowack, and R.H. Baker, J. Org. Chem. 33:610 (1968).

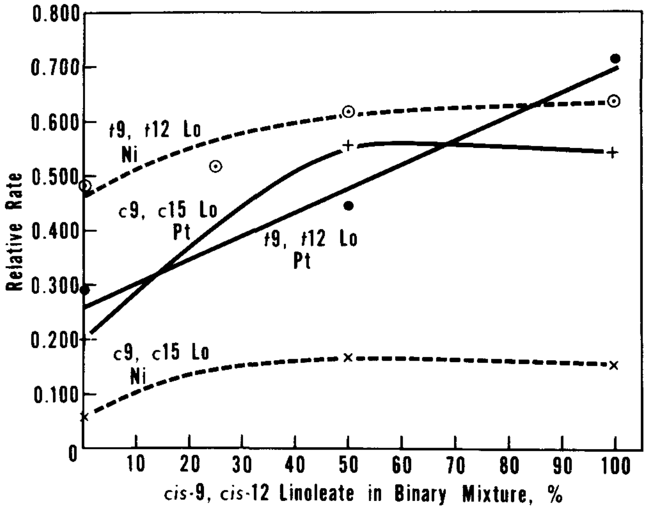

FIG. 2. Relative rates vs mass composition.

TABLE IV

Relative Rates[a] of Isomers from Consecutive Hydrogenations

Hydrogenation	Pt	Ni
$k_{trans\text{-}9,trans\text{-}12}/k_{cis\text{-}9,cis\text{-}12}$	1.00	0.77
$k_{cis\text{-}9,cis\text{-}15}/k_{cis\text{-}9,cis\text{-}12}$	0.86	0.31

[a] Rate of each isomer is calculated from the average of three slopes from the plots of the successive hydrogenations.

[Received February 10, 1975]