

Hydrogenation of *cis*-9,*cis*-12-, *cis*-9,*trans*-12- and *trans*-9,*trans*-12- Octadecadienoates¹

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ABSTRACT

The products formed by hydrogenation of methyl *cis*-9,*trans*-12- and *trans*-9,*trans*-12-octadecadienoates with nickel and platinum catalysts have been compared with those from methyl esters of the naturally occurring all-*cis* linoleate. Hydrogen uptake is slower for the *trans* isomers. Much of the monoene consisted of esters with double bonds at the 9 and 12 positions with their original geometric configurations. Monoenoic esters with double bonds at the 10 and 11 positions were predominately *trans* and apparently formed by conjugation before hydrogenation. Nickel produced more isomerization than platinum but less than previously reported for copper. With both catalysts hydrogenation proceeded both directly and through conjugated intermediates, in contrast to copper in which all hydrogenation is believed to follow conjugation.

INTRODUCTION

Although the products formed by partial hydrogenation of methyl *cis*-9,*cis*-12-linoleate have been studied for various conditions of hydrogenation (1-3), less is known of the products formed from other octadecadienoate isomers. During hydrogenation of vegetable oils dienes containing isolated *trans* bonds, as well as conjugated dienes, may be formed both by isomerization of linoleate and by isomerization and reduction of linolenate. Information about the subsequent reactions of such intermediates is necessary for understanding the pathways and mechanisms that lead to the final mixture of partially hydrogenated material.

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A study of the products from some conjugated octadecadienoates has recently been published (4). In this paper we present information about the products from hydrogenation of some octadecadienoates containing isolated *trans* bonds.

EXPERIMENTAL PROCEDURES

Materials

Methyl *cis*-9,*cis*-12-linoleate was prepared from safflower methyl esters by counter double current distribution (5). The *trans*-9,*trans*-12-isomer was prepared by nitrous acid isomerization of methyl linoleate (6) and separated by argentation countercurrent distribution (7). To prepare methyl *cis*-9,*trans*-12-linoleate, methyl ricinoleate was dehydrated by the estolide procedure of Schneider et al. (8); the product was fractionated by silver resin chromatography (9).

The platinum catalyst was Engelhard Industries 5% platinum on carbon. The commercial nickel catalyst, G-15, came from Girdler Catalysts Department, Chemtron Corp.

Hydrogenations

Hydrogenations were carried out in the precision hydrogenator described by Rohwedder (10), but with a glass vessel instead of his metal one. Approximately 1 mole hydrogen was added per mole of ester. About 300 mg samples were hydrogenated with ca. 0.5% nickel at 140 C or 0.09% platinum at 50 C.

Fractionation and Analysis

Hydrogenated samples were separated into diene, monoene and stearate fractions by chromatography on a rubber column (11). Monoene was separated into *cis* and *trans* fractions on a silver resin column (9). The gas chromato-

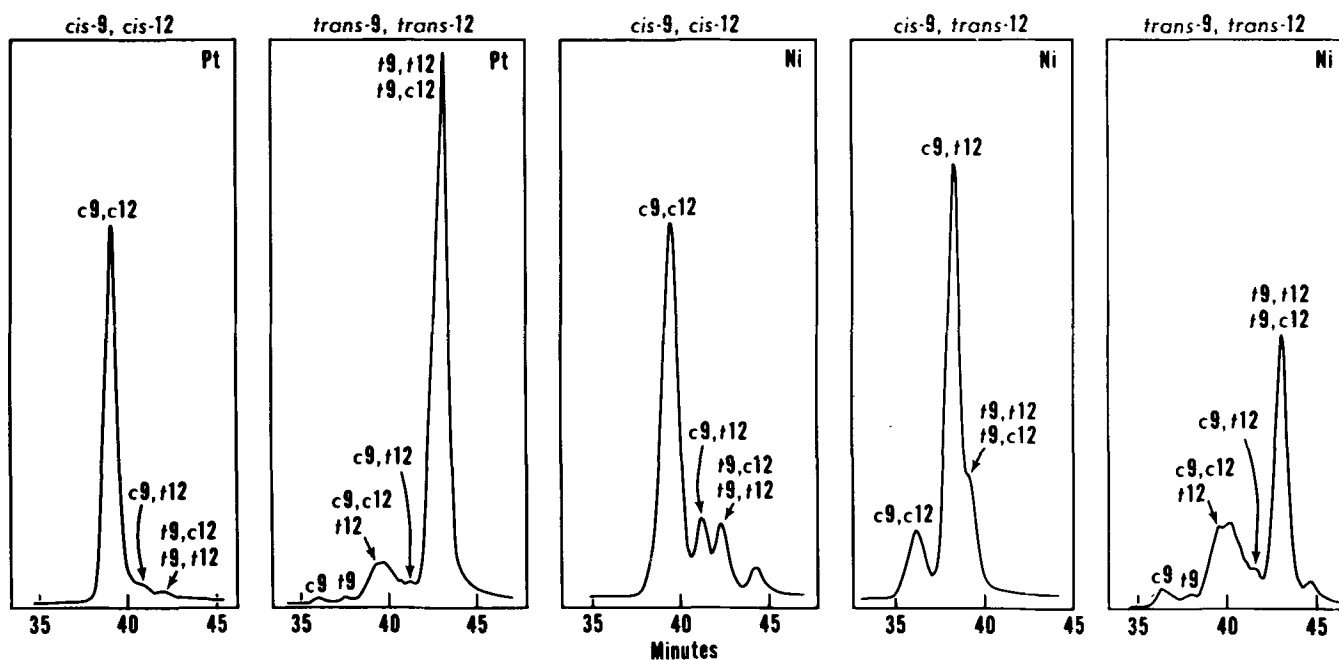


FIG. 1. Capillary gas chromatograms of diene fractions from partially hydrogenated methyl octadecadienoates.

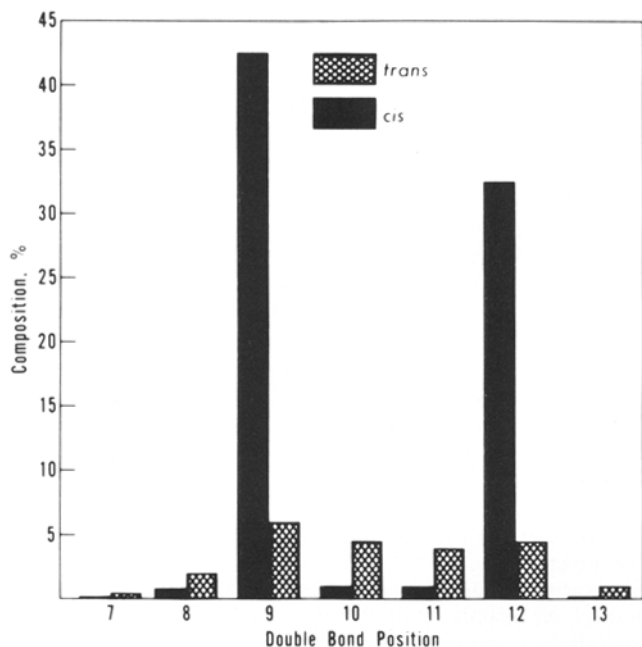


FIG. 2. Double bond positions in monoene from methyl *cis*-9,*cis*-12-octadecadienoate hydrogenated with platinum catalyst.

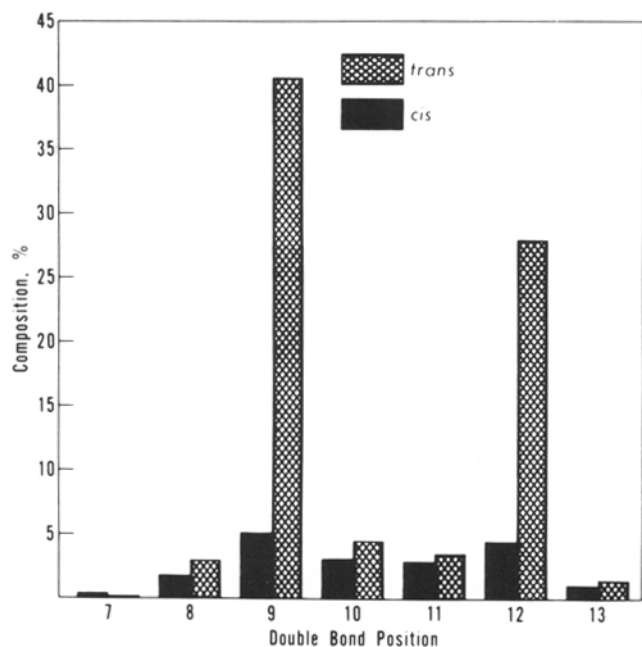


FIG. 3. Double bond positions in monoene from methyl *trans*-9,*trans*-12-octadecadienoate hydrogenated with platinum catalyst.

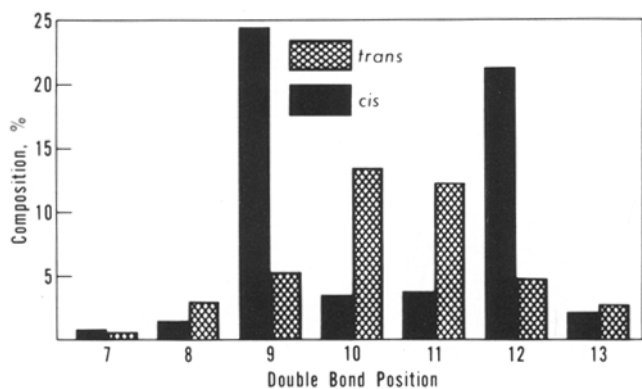


FIG. 4. Double bond positions in monoene from methyl *cis*-9,*cis*-12-octadecadienoate hydrogenated with nickel catalyst.

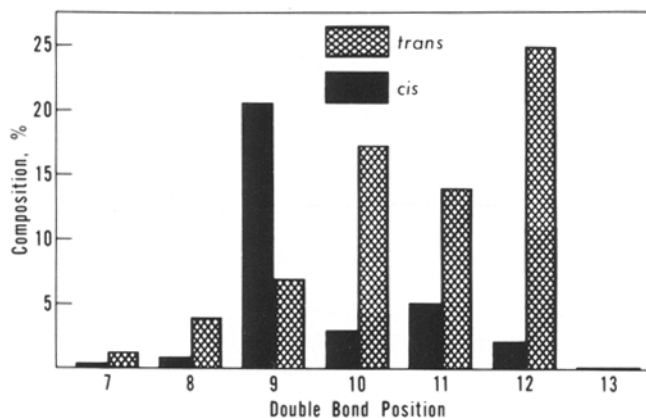


FIG. 5. Double bond positions in monoene from methyl *cis*-9,*trans*-12-octadecadienoate hydrogenated with nickel catalyst.

graphic compositions in Table I were measured on an ESSS-X column and are area per cent as determined with a radium D argon detector. The *trans* content was measured by IR with methyl elaidate taken as 100%. Double bond location in the monoenes was determined by ozonization and gas chromatographic analysis of products (12).

The capillary gas chromatograms in Figure 1 were run on 150 ft x 0.01 in. ID polyphenyl ether column at 190 C.

RESULTS AND DISCUSSION

Recorder charts of hydrogen uptake vs. time (10) produced straight lines indicating zero order over nearly all the reaction. Rates of hydrogen uptake for nickel were as follows: *cis*-9,*cis*-12 3.13 ml/min; *cis*-9,*trans*-12 1.25 ml/min; *trans*-9,*trans*-12 1.44 ml/min, and for platinum: *cis*-9,*cis*-12 1.15 ml/min; *trans*-9,*trans*-12 0.43 ml/min. Although hydrogen uptake rates commonly vary somewhat from run to run, the all-*cis* ester always hydrogenated over twice as fast as the *trans*-containing esters. This difference in hydrogenation rates is consistent with that found for monoenoic esters (13). The differences between rates with nickel and platinum will of course vary with differences in catalyst concentration and temperature.

Composition of the hydrogenated products is detailed in Table I.

The IR absorption *trans* values may be compared with values of 162.9% *trans* for the original *trans,trans* ester and 75.8% *trans* for the *cis,trans* ester. These values are consistent with earlier observations that absorption per double bond is less for methylene-interrupted dienes than for methyl elaidate (7,14). Since the UV absorption at 233 μ is low with both catalysts, there is no appreciable accumulation of conjugated esters.

Values in Table I show that more *trans* bonds formed from *cis,cis* linoleate with nickel than with platinum;

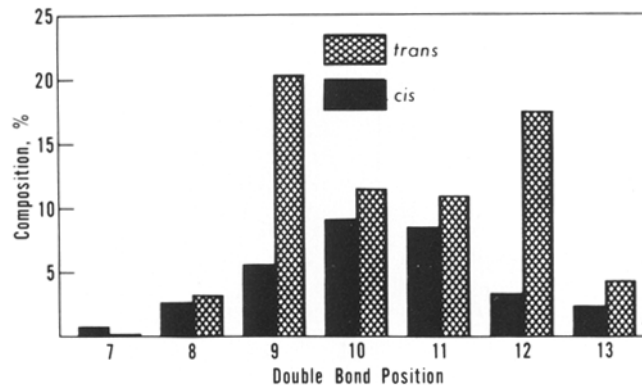


FIG. 6. Double bond positions in monoene from methyl *trans*-9,*trans*-12-octadecadienoate hydrogenated with nickel catalyst.

TABLE I

Analysis of Hydrogenated Esters from Methyl Octadecadienoate Isomers

Ester	Catalyst	<i>trans</i> , %	a_{233}	Gas liquid chromatographic composition and analysis of fractions					
				Stearate, %	Monoene		Diene		a_{233}
					%	<i>trans</i> , %	%	<i>trans</i> , %	
<i>cis</i> -9, <i>cis</i> -12	Ni	42		6.9	80.5	42.6	12.6	43	1.6
<i>cis</i> -9, <i>trans</i> -12	Ni	68	0.29	4.4	57.1	62.9	38.5	89	0.17
<i>trans</i> -9, <i>trans</i> -12	Ni	69	0.09	13.2	70.8	67.7	16.0	139	1.1
<i>cis</i> -9, <i>cis</i> -12	Pt	10	0.52	22.8	46.8	22.2	30.0	0	1.50
<i>trans</i> -9, <i>trans</i> -12	Pt	79	0.25	20.9	54.7	81.2	24.4	151	1.46

however with the *trans,trans* linoleate the *trans* content of both diene and monoene fractions is less with nickel than with platinum. Thus nickel produced more *cis,trans* isomerization than platinum.

Peaks in capillary gas chromatograms (Fig. 1) of the diene fractions were identified by comparison of equivalent chain lengths with those of known compounds (15). In all curves the large peak corresponds to the starting diene. Small peaks correspond in position to other isomers. With both catalysts the *trans,trans* linoleate produced a small unresolved double peak. One part corresponds to *cis*-9,*cis*-12-linoleate; the other is unidentified. Also, with nickel both *cis,cis* and *trans,trans* esters produced a small unidentified peak eluted more slowly than the 9,12-linoleates.

Double bond distributions of the monoene fractions are shown in Figures 2-6. With platinum, ca. 70% of the monoene esters has a double bond position and a configuration corresponding to the original double bonds in the diene. With nickel the value is ca. 40%. These values suggest that a large part of the diene was reduced directly without going through a conjugated intermediate. Under similar reaction conditions in previous work (4) we showed that with conjugated esters and platinum catalyst about one-third of the reduction was by 1,4-addition. If conjugated intermediates are reduced the same way here, then 15% of the unconjugated *cis,cis* and 20% of the unconjugated *trans,trans* were hydrogenated through a conjugated intermediate. With nickel we found slightly less 1,4-addition. If one assumes that 25% of a conjugated ester is reduced by 1,4-addition, one may calculate that with a nickel catalyst ca. 54% of the unconjugated *cis,cis* 63% of the *cis,trans* and 64% of the *trans,trans* linoleate were hydrogenated through a conjugated intermediate.

The small amounts of double bonds found outside the 9- to 12-carbon region probably result from half hydrogenation-dehydrogenation reactions and from monoene isomerization (16). Although monoene isomerization occurring within the 9- to 12-carbon region introduces some error in the calculations, it should not greatly affect the conclusions. These double bond distributions contrast sharply with those found for a copper-catalyzed hydrogenation (17) in which all the reduction is believed to involve conjugated intermediates.

The data presented here suggest similarities between the process of conjugation that accompanies hydrogenation and that which is catalyzed by alkali. Both alkali isomerization (18) and catalytic hydrogenation are faster with *cis* than with *trans* isomers. Also, if conjugation on the catalyst surface follows the same rules as alkali conjugation (19) (a *cis* bond becomes *trans* when it moves; a *trans* bond can become either *cis* or *trans*), the lower *trans* content of 10- and 11-monoenes from *trans,trans* dienes than of those from *cis,cis* dienes, and the lower *trans* content of 11- than of 10-monoene from *cis*-9,*trans*-12-linoleate, would be expected.

These results, insofar as they are comparable, confirm earlier work on *cis*-9,*cis*-12-linoleate (1-3). The double bond distributions with nickel are like those found by Cousins et al. (2) at similar temperatures. At higher temperatures they found more double bonds in the 10 and 11 positions, indicating that a greater part of the oil goes through a conjugated intermediate. The great difference with platinum catalysts between these latest results and those of Cousins and his coworkers is undoubtedly caused by differences in temperature.

Apparently then octadecadienoates containing isolated *trans* bonds are hydrogenated in much the same way as naturally occurring *cis*-9,*cis*-12-linoleate. Unlike hydrogenations with copper catalysts, reduction with nickel and platinum proceeds both directly and through conjugated intermediates. Esters containing *trans* bonds are reduced more slowly, but the proportion going through conjugated intermediates, the amount of positional and geometric isomerization, and the course of the reactions are very similar.

ACKNOWLEDGMENTS

J. Snyder did much of the experimental work and A.E. Johnston did the double bond location.

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