

# Selective Hydrogenation With Copper Catalysts:

## III. Hydrogen Addition and Isomerization<sup>1</sup>

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### Abstract

$\beta$ -Eleostearate was found to be reduced by 1,6 addition of hydrogen. Because of the extensive isomerization of conjugated trienes during hydrogenation, the occurrence of 1,2 and 1,4 addition reactions could not be proven. Conjugated dienes were reduced by both 1,2 and 1,4 addition of hydrogen. The double bond distribution in the products formed from linoleate, linolenate and their isomers was consistent with the assumption that the double bonds in polyunsaturated fatty esters conjugate and then add hydrogen. Extensive isomerization (positional and geometric) of the conjugated double bond systems occurred during hydrogenation. Monoenes were not isomerized under similar conditions of hydrogenation. Since double bond distribution in monoenes formed from linoleate and alkali-isomerized linoleate was identical, indications are that conjugation precedes hydrogenation.

### Introduction

Conjugated dienes were the major products of hydrogenation of linolenate with copper chromite (1). Conjugation of the double bonds in polyunsaturated esters was found to precede hydrogenation (2). The mechanism of hydrogen addition to conjugated double bond systems in the presence of copper chromite is described in this report.

### Experimental Procedures

The preparation and hydrogenation of some of the polyunsaturated esters were reported in the preceding paper (2). Linolelaidate was prepared by isomerizing linoleate with nitrous acid (3). Linolelaidate, which was further purified by chromatography on a silver-saturated resin column (4), contained 167% *trans* referred to elaidate. Alkali-isomerized linoleate was equilibrated to form all-*trans* conjugated dienes by iodine and light (5). All-*trans* conjugated dienes were obtained by chromatography of the equilibrated mixture on a silver resin column.  $\beta$ -Eleostearate was prepared according to the procedure of Hoffmann et al. (6). *Trans*-9,*trans*-11-octadecadienoate was synthesized from castor oil (7).

The hydrogenated products were separated according to unsaturation by reverse phase chromatography on a rubber column (8). Monoenes were further separated into *cis* and *trans* isomers, and conjugated dienes were separated into *cis,trans* and *trans,trans* isomers on a silver-saturated resin column (4). The location of the double bonds in various fractions was determined by reductive ozonolysis (9). Aldehydes, aldehyde esters and dialdehydes were analyzed as reported in Part I (1).

### Results and Discussion

$\beta$ -Eleostearate was 50% reduced with copper chromite catalyst at 150 C and atmospheric hydrogen

pressure. The products were separated and analyzed by reductive ozonolysis (Fig. 1). Gas liquid chromatography of the unreacted triene showed both  $\alpha$ - and  $\beta$ -eleostearates, as well as an unidentified peak that was probably a geometrical isomer. The conjugated triene system was extensively isomerized as seen from Figure 1. Only 28.5% of the unreacted conjugated triene had its double bonds in the original 9,11,13 position. The rest was isomerized from  $\Delta^{5,7,9}$  to  $\Delta^{12,14,16}$  isomers. If reduction of  $\beta$ -eleostearate takes place by 1,4 addition of hydrogen, methylene-interrupted dienes should result. The fact that only conjugated dienes were formed seems to rule out this mechanism. However, the possibility of 1,4 addition followed by conjugation on the catalyst surface cannot be discounted.  $\Delta^{9,11}$  and  $\Delta^{11,13}$  isomers should be formed in equal amounts if 1,2 addition of hydrogen takes place, whereas  $\Delta^{10,12}$  should result by 1,6 addition.  $\Delta^{10,12}$  Conjugated diene is the major product formed, which indicates that hydrogenation occurred by 1,6 addition. The formation of  $\Delta^{10,12}$  isomer as a major product is not unequivocal evidence and 1,2 addition cannot be entirely ruled out. However, the principle products can be explained by invoking 1,6 addition of hydrogen as a major pathway. If hydrogenation were stopped earlier, perhaps at 5% or 10% reduction, less isomerization of the triene and more of the  $\Delta^{10,12}$  diene would have resulted.

The results obtained with *trans*-9,*trans*-11-octadecadienoate, which was 40% reduced, are shown in Figure 2. Some *trans,trans* conjugated diene was isomerized to *cis,trans* isomer (*trans,trans/cis,trans* = 2.7). Little, if any, of the *cis,cis* isomer (<5%) was formed. The unreacted conjugated dienes were extensively isomerized during hydrogenation. In both the *trans* and *cis* monoene fractions (*trans/cis* in monoene = 2.0),  $\Delta^{10}$  monoene is the predominant isomer. These results can be explained by assuming

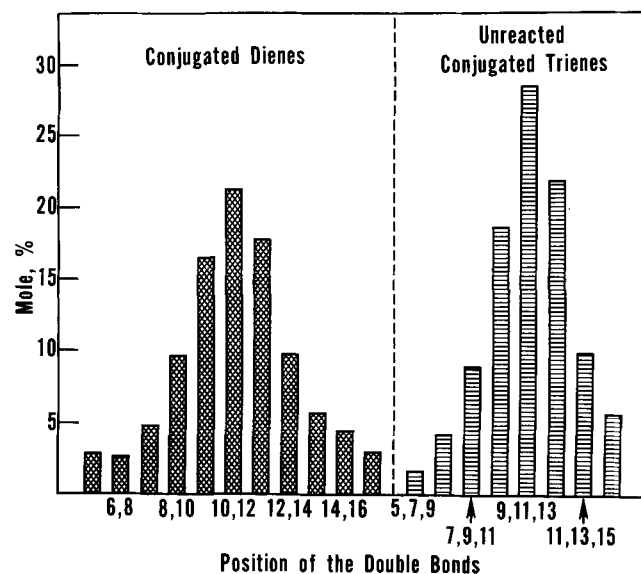


Fig. 1. Isomerization during hydrogenation of  $\beta$ -eleostearate.

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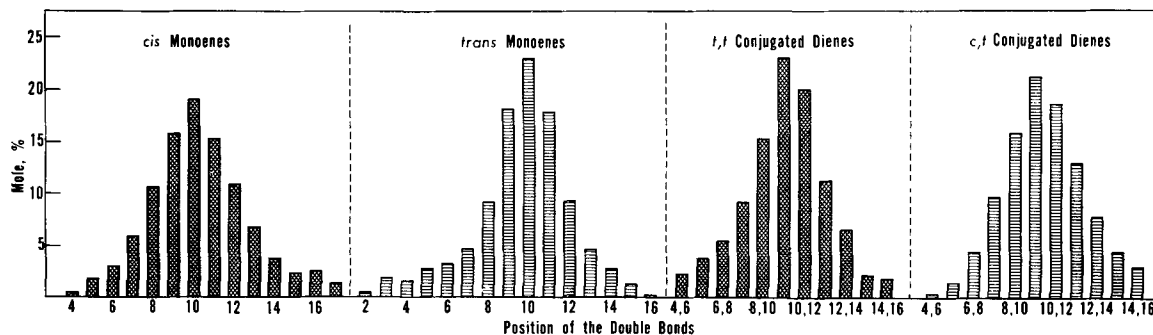


FIG. 2. Isomerization during hydrogenation of *trans*-9,*trans*-11-octadecadienoate.

1,4 addition of hydrogen to *trans,trans* conjugated dienes. However, 1,2 addition cannot be ruled out. The formed monoene will have either *trans* or *cis* configuration depending upon the *transoid* (*anti*) or *cisoid* (*syn*) conformation of the conjugated diene (10). The monoene when once formed will not be further isomerized by the catalyst. Methyl oleate treated under similar conditions of hydrogenation produced only 4% *trans* isomers and more than 96% of the double bonds were at the 9,10 position. Thus each monoene isomer represented in Figure 2 resulted from hydrogenation of conjugated diene and not by isomerization of the monoene.

The results of hydrogenation of *trans*-10,*cis*-12-octadecadienoate are depicted in Figure 3. Hydrogenation was stopped at 20% reduction to minimize isomerization. Even at this early stage of hydrogenation, *cis,trans* conjugated diene was converted to *trans,trans* isomer (*trans,trans*/*cis,trans* = 2.0). The interpretation of the results is complicated since *trans,trans* conjugated diene is the predominant isomer even at an early stage of hydrogenation. However, since  $\Delta^{12}$  monoene is the predominant *cis* isomer, 1,2 addition of hydrogen to *cis,trans* conjugated diene must have taken place.  $\Delta^{10}$  Monoene would be expected as the predominant isomer in *trans* monoenes if 1,2 addition were exclusively operating.  $\Delta^{11}$  Monoene is the major isomer in the *trans* fraction because the *trans,trans* isomer that is formed by isomerization will form monoene by 1,4 addition. However, 1,4 addition to *cis,trans* conjugated dienes cannot be excluded by these results.

In Figures 4 and 5 are shown the results of hydrogenation of alkali-isomerized linoleate and linoleate (50% reduction). Alkali-isomerized linoleate consists of *cis*-9,*trans*-11 and *trans*-10,*cis*-12-octadecadienoate mixture (11). Hydrogenation by 1,2 addition should result in  $\Delta^9$  and  $\Delta^{12}$  *cis* monoenes and  $\Delta^{10}$  and  $\Delta^{11}$  *trans* monoenes. However, isomerization to *trans,trans* dienes and subsequent hydrogenation by 1,4 addition should result in  $\Delta^{10}$  and  $\Delta^{11}$  monoenes with *cis* as well as *trans* configuration. As a result of both these reactions occurring simultaneously, one would expect

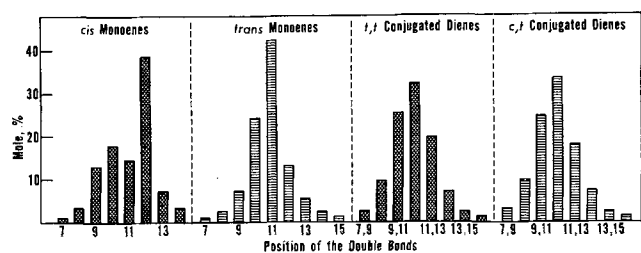


FIG. 3. Isomerization during hydrogenation of *trans*-10,*cis*-12-octadecadienoate.

$\Delta^{10}$  and  $\Delta^{11}$  *trans* monoenes and  $\Delta^9$ ,  $\Delta^{10}$ ,  $\Delta^{11}$  and  $\Delta^{12}$  *cis* monoenes. The results represented in Figure 4 are consistent with the proposed mechanism of hydrogen addition. The fact that the double bond distribution in monoenes formed from linoleate (Fig. 5) is almost identical with the monoenes formed from alkali-isomerized linoleate, indicates that the double bonds in linoleate were first conjugated before hydrogenation. While unreacted conjugated dienes are extensively isomerized during hydrogenation (Fig. 4), little, if any, alteration occurred to methylene-interrupted double bonds. In the diene fraction from unreacted linoleate, conjugated dienes, which amounted to 10% of the diene, were extensively isomerized. The remainder had double bonds at the 9 and 12 positions. The double bond distribution of monoenes formed from linoleate (Fig. 6) is also consistent with the proposed conjugation mechanism. The double bond that moved to a conjugated system will assume either *trans* or *cis* configuration (11) and further isomerization by the catalyst favors *trans,trans* conjugated dienes ( $\Delta^{9,11}$  and  $\Delta^{10,12}$ ). Thus one would expect  $\Delta^{10}$  and  $\Delta^{11}$  monoenes in both the *cis* and *trans* monoene fractions. From Figure 6 it can be seen that  $\Delta^{10}$  and  $\Delta^{11}$  monoenes are the predominant isomers. The unreacted diene, which contained less than 1% conjugation, consisted of linoleate (*trans*-9,*trans*-12-octadecadienoate). The double bond distribution of monoenes from all-*trans*  $\Delta^{9,11}$  and  $\Delta^{10,12}$ -octadecadienoate mixture (Fig. 7) is almost identical to that obtained from linoleate. The double bond distribution patterns obtained with linoleate, linoleate and conjugated dienes (Fig. 4-7) provide strong evidence that conjugation of the double bonds in linoleate precedes hydrogenation.

The composition of monoenes and dienes formed during hydrogenation of  $\Delta^{5,9,12}$  and  $\Delta^{3,9,12}$  triene isomers (Fig. 8) is also consistent with the conjugation mechanism. The methylene-interrupted double bonds first conjugate to form two conjugated diene-trienes (for example  $\Delta^{5,9,11}$  and  $\Delta^{5,10,12}$  isomers). Hydrogenation of these conjugated systems should produce  $\Delta^{5,10}$  and  $\Delta^{5,11}$  dienes from  $\Delta^{5,9,12}$  triene and  $\Delta^{3,10}$  and  $\Delta^{3,11}$  dienes from  $\Delta^{3,9,12}$  triene as the predominant isomers. These are indeed the major products in the dienes. Other diene isomers evolved from isomerization of the conjugated double bonds followed by hydrogenation. Every diene molecule had one double bond at the 5,6 position (3,4 position with  $\Delta^{3,9,12}$  triene) since the isolated double bond does not hydrogenate or isomerize. If the conjugated double bonds moved toward the isolated double bond, then conjugated triene would result ( $\Delta^{5,7,9}$  from  $\Delta^{5,9,12}$  triene). Hydrogenation by 1,6 addition results in conjugated diene which, in turn, will be reduced by 1,4 addition to form  $\Delta^7$  monoene as the major product.

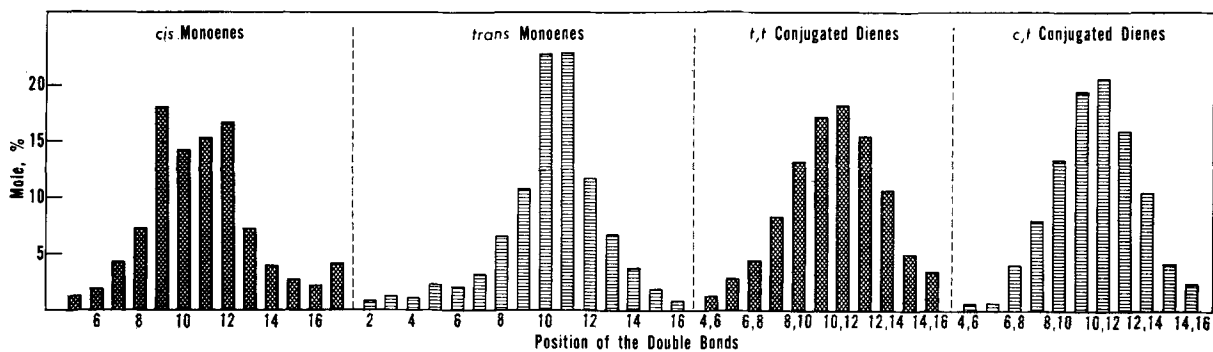


FIG. 4. Isomerization during hydrogenation of alkali-isomerized linoleate.

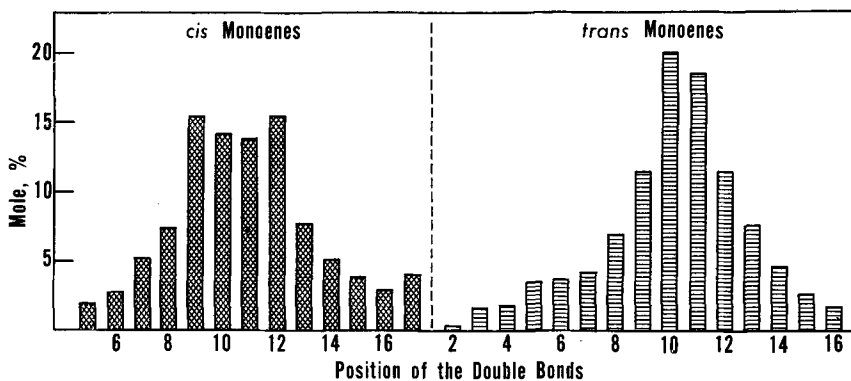


FIG. 5. Double bond distribution of monoenes formed from linoleate.

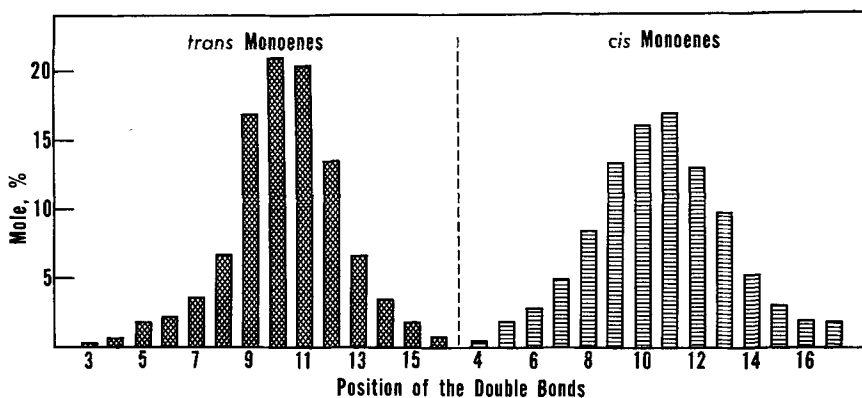


FIG. 6. Double bond distribution of monoenes formed from linoleaidate.

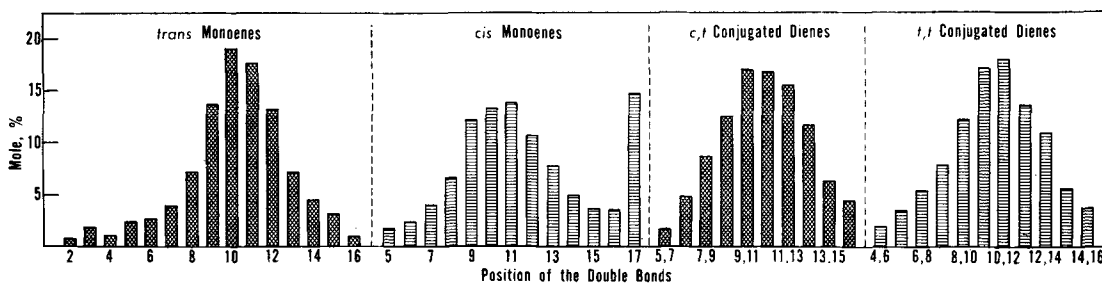


FIG. 7. Isomerization during hydrogenation of all-trans  $\Delta^{9,11}$  and  $\Delta^{10,12}$ -octadecadienoate mixture.

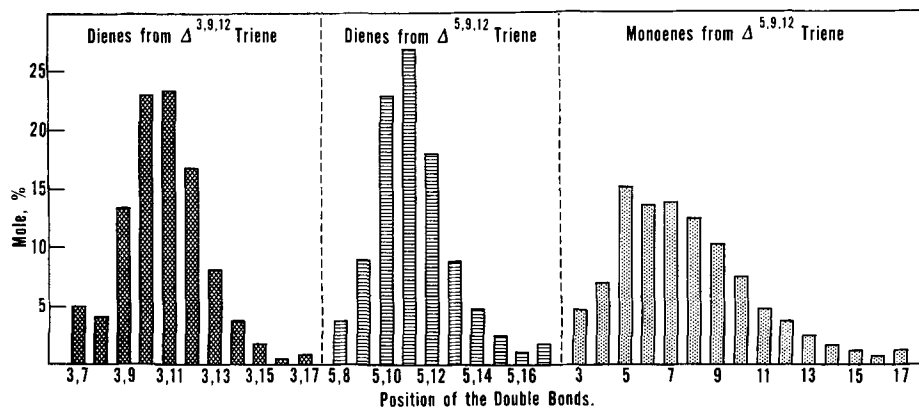


FIG. 8. Composition of the monoenes and dienes formed during hydrogenation of  $\Delta^{5,9,12}$  and  $\Delta^{3,9,12}$ -octadecatrienoates.

However, because conjugated trienes isomerize during hydrogenation and the formed conjugated dienes further isomerize during hydrogenation to monoenes, the double bonds in monoenes are quite scattered. Most of the double bonds are found in the 5 to 9 positions (Fig. 8) whereas the monoenes from linolenate have double bonds from the 9 to 15 positions (1).

The composition of aldehyde esters and dialdehydes of dienes formed during hydrogenation of  $\Delta^{9,11,15}$  and  $\Delta^{9,13,15}$ -octadecatrienoate mixture is given in Figure 9. Determination of the structure of dienes is difficult; but  $\Delta^{9,15}$  diene is present. Also, since the infrared spectrum of dienes shows a strong absorption typical of the vinyl group, the presence of  $\Delta^{9,17}$  diene is indicated. The composition of dialdehydes indicated that the dienes had widely separated double bonds. These dienes were not conjugated by alkali (2). In the hydrogenation of linolenate, it has been

proposed (2) that nonconjugatable dienes are formed from conjugated diene-triene. The ozonolysis products of diene from linolenate had a similar composition to that shown in Figure 9. In the conjugated diene-triene mixture, the diene formed from  $\Delta^{9,13,15}$  isomer should always contain the first double bond at the 9,10 position since it is the isolated double bond. Thus, a large amount of the nonconjugated diene is expected to contain the first unsaturation at the 9,10 position. Actually 67.5% of the nonconjugated diene (Fig. 9) was found to have its first double bond at the 9,10 position.

The composition of the products formed during hydrogenation of several isomers studied provides further evidence for conjugation mechanism. While the evidence presented for the mechanism of hydrogen addition to conjugated double bonds is not unequivocal, data do provide strong evidence. Further proof of this mechanism might come from deuterium tracer studies.

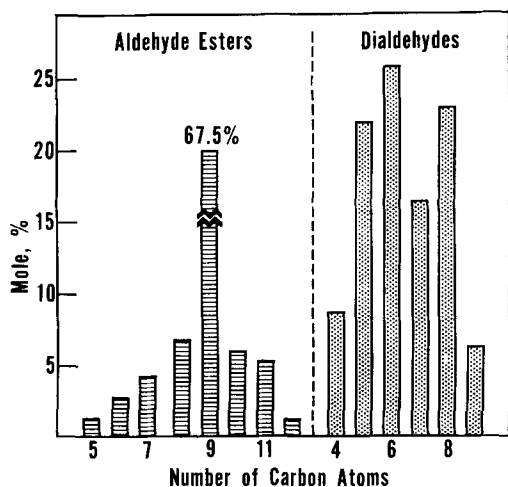


FIG. 9. Ozonolysis of dienes formed during hydrogenation of  $\Delta^{9,11,15}$  and  $\Delta^{9,13,15}$ -octadecatrienoate mixture.

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