Hydrogenation of Alkali-Conjugated Linoleate: Isomeric Monoene Profiles Obtained with Nickel, Palladium and Platinum Catalysts

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ABSTRACT

Alkali-conjugated linoleate (*cis*-9,*trans*-11- and *trans*-10,*cis*-12-octadecadienoate) was hydrogenated with nickel, palladium and platinum catalysts. The *trans* and *cis* monoenes formed during reduction were isolated, and their double bond distribution was determined by reductive ozonolysis and gas liquid chromatography. About 44-69% of the monoenes were composed of Δ^{10} and Δ^{11} *trans* monoene isomers, whereas the Δ^{9} and Δ^{12} *cis* monoenes amounted to 20-26%. With nickel catalyst, composition of monoene isomers remained the same, even when the hydrogenation temperature was increased. The monoene isomer profiles between nickel and palladium catalysts were indistinguishable. Isomerization of monoenes with platinum catalyst was suppressed at 80 psi. The position of the double bonds in unreacted conjugated diene was always retained, except with nickel at both temperatures and with platinum at 150 C when a slight migration occurred. Geometrical isomerization to *trans,trans*-conjugated diene was observed in the unreacted diene with nickel (ca. 15% of diene) at both 100 C and 195 C, and with platinum (ca. 7% of diene) at 150 C.

INTRODUCTION

The selective hydrogenation of linoleate over oleate with heterogeneous catalysts, particularly nickel, is generally attributed to the ability of these catalysts to conjugate methylene-interrupted double bonds (1-4). The products from linoleate hydrogenation have been characterized (3,4). We wish to report on the hydrogenation and characterization of products from alkali-conjugated linoleate, the most likely form of conjugation to occur on catalyst surfaces.

EXPERIMENTAL PROCEDURES

Alkali isomerization of methyl linoleate (Hormel Institute) was carried out under nitrogen at 180 C for 30 min with 25% KOH in ethylene glycol. The isomerized acids were isolated after acidification of the reaction mixture. The acids were converted to methyl esters with methanolic hydrochloric acid and 2,2-dimethoxy propane (5). Gas chromatography (GC) of vacuum-distilled esters showed ca. 3% unreacted diene, 2% *trans,trans*-conjugated diene and 95% *cis,trans*-conjugated diene. Reductive ozonolysis (6) indicated ca. 1% $\Delta^{8,10}$; 55% $\Delta^{9,11}$; 43% $\Delta^{10,12}$ and 1% $\Delta^{11,13}$ conjugated isomers. Apparently the 12,13 double bond in linoleate shifts preferentially to give more $\Delta^{9,11}$ isomer than the $\Delta^{10,12}$.

Hydrogenations were carried out at atmospheric pressure in a manometric apparatus described previously (7) with nickel (G-49A Girdler catalyst) at 100 C and 195 C; with 5% palladium on carbon (Baker & Co.) at 25 C; and with 5% platinum on carbon (Engelhard Industries) at 35 C and 150 C. One run was made at 80 psi with platinum catalyst in pentane-hexane solvent contained in a 150 ml magnetically stirred Magnadash autoclave. After an uptake of ca. 0.4-1.3 mol hydrogen per mole of ester, the composition of the product was determined by GC. The product was separated into dienes, monoenes and stearate by reverse phase chromatography (8). The monoenes were further separated into *trans* and *cis* fractions on a silver-exchanged resin column (9). The percentage *trans* in monoene was calculated from the weight recovery of *trans* and *cis* monoenes. The results are shown in Table I.

RESULTS AND DISCUSSION

At atmospheric pressure, selectivity for the reduction of conjugated diene increased when the hydrogenation temperature increased, as evidenced by decreased stearate formation. The percentage *trans* in the monoene product with nickel and platinum catalysts remained the same, regardless of hydrogenation temperature. Nickel and palladium at atmospheric pressure and platinum at 80 psi showed more *trans* in monoenes than platinum at atmospheric pressure. GC indicated that ca. 15% of the unreacted conjugated diene was isomerized to *trans,trans*-conjugated dienes with nickel at both temperatures. Platinum at the higher temperature showed slight (~7%) isomerization to *trans,trans*-conjugated diene, whereas palladium and platinum at 35 C produced none. Ozonolysis of the unreacted

TABLE I

Fatty Acid Composition of Products Formed during Partial Hydrogenation of Alkali-Conjugated Linoleate

		Composition, wt %			
Catalyst	Temperature, C	CD[a]	D	M	St
Nickel	100	46.8	2.9	50.0 (73)[b]	0.3
Nickel	195	59.8	3.3	36.9 (74)	Trace
Palladium	25	57.6	2.4	39.0 (73)	1.0
Platinum	35	54.8	1.3	31.5 (65)	12.4
Platinum	150	44.7	2.4	44.9 (65)	8.0
Platinum	25[c]	7.3	--	52.7 (75)	40.0

[a] CD, conjugated diene; D, diene; M, monoene; St, stearate.

[b] Number in parentheses represents the percentage *trans* in monoene.

[c] At 80 psi.

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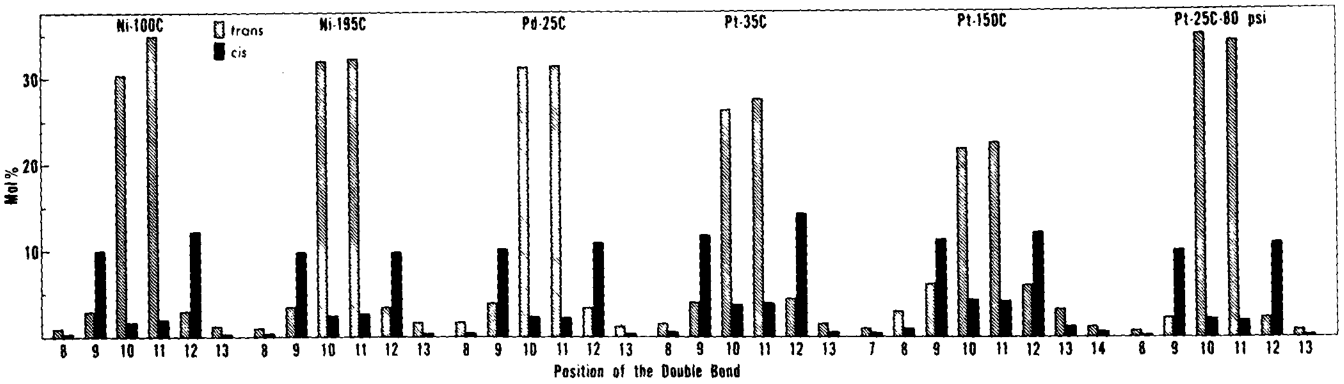

FIG. 1. Composition of monoene isomers formed during hydrogenation of alkali-conjugated linoleate.

conjugated dienes indicated migration of double bonds with nickel catalyst at both temperatures and with platinum catalyst at 150 C. The $\Delta^{8,10}$ + $\Delta^{11,13}$ isomers increased from 2 to 4% with nickel at 100 C; to 7% with nickel at 195 C; and to 4% with platinum at 150 C.

The isomeric monoene distributions calculated from reductive ozonolysis (6) of the *trans* and *cis* monoene fractions are plotted in Figure 1. Δ^9 and Δ^{12} *cis*-monoenes are formed by 1,2 addition, whereas Δ^{10} and Δ^{11} *trans*-monoenes are formed by both 1,2- and 1,4-addition reactions. There was no significant difference in the monoene profiles between nickel at 100 C and 195 C. The products were quite similar with either palladium or nickel catalysts. Platinum catalyst at 35 C formed less Δ^{10} and Δ^{11} *trans* isomers and more Δ^9 and Δ^{12} *cis* isomers than nickel and palladium catalysts. Increasing hydrogenation temperature with platinum decreased the amount of Δ^{10} and Δ^{11} *trans*-monoenes (with concomitant increase in Δ^9 and Δ^{12} *trans*-monoenes) due to increased isomerization of monoenes. High pressure reduction with platinum suppressed isomerization of monoenes. The higher amounts of Δ^{10} and Δ^{11} *trans*-monoenes, with concomitant lower amounts of Δ^9 and Δ^{12} *cis*-monoenes than those from atmospheric pressure hydrogenation, might have resulted from preferential hydrogenation of *cis*-monoenes over *trans*-monoenes (10).

When monoenes are formed by addition reaction, there is always the possibility of further addition to form stearate or isomerization (positional and geometrical) before they are desorbed from the catalyst surface. From the profiles with nickel catalyst it would appear that further isomerization of monoenes is suppressed by conjugated dienes. The small amounts of Δ^9 and Δ^{12} *trans*-monoenes are probably formed from isomerized *trans,trans*-conjugated dienes. Δ^{10} and Δ^{11} *cis*-monoenes are formed by 1,4 addition to conjugated dienes in a cisoid configuration. Δ^8 and Δ^{13} isomers are formed from $\Delta^{8,10}$ and $\Delta^{11,13}$ isomers. With palladium catalyst, however, monoenes appear to be further isomerized before they are desorbed. Because no isomerization of unreacted conjugated dienes was observed, Δ^9 and Δ^{12} *trans*-monoenes must arise by isomerization of monoenes. The formation of considerable amounts of stearate with platinum catalyst (Table I) indicates isomerization of monoenes, which is known to occur during reduction of monoenes (11). At 150 C, even positional isomerization is considerable, as evidenced by the presence of Δ^7 and Δ^{14} monoene isomers.

By comparing these monoene profiles with those obtained from methyl linoleate under similar conditions of hydrogenation (12), it is possible to calculate the amount of linoleate that was reduced through a conjugated intermediate. The ratio of the Δ^{10} + Δ^{11} *trans* monoenes from linoleate hydrogenation to those from alkali-conjugated linoleate represents the fraction of linoleate reduced through conjugation. Hydrogenations carried out under similar conditions of temperature and pressure (12) indicate that 57% of the linoleate was reduced through a conjugated intermediate with nickel at 195 C. The respective percentages for palladium and platinum catalysts were 51 and 25.

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