Catalytic Hydrogenation of Linoleic Acid on Nickel, Copper, and Palladium

Yoshie Kitayama^{a,*}, Masahiro Muraoka^a, Megumi Takahashi^a, Tatsuya Kodama^a, Hirofumi Itoh^b, Eriko Takahashi^b, and Mutsuo Okamura^c

^aDepartment of Chemistry and Chemical Engineering, Niigata University, Ikarashi Niigata 950-21, Japan, ^bNikki Chemical Co. Ltd. Niitsu Plant Office, Niitsu City, 956, Japan, and ^cDepartment of Chemistry, Faculty of Science, Niigata University, Ikarashi Niigata 950-21, Japan

ABSTRACT: The catalytic activity and selectivity for hydrogenation of linoleic acid were studied on Ni, Cu, and Pd catalysts. A detailed analysis of the reaction product was performed by a gas-liquid chromatograph, equipped with a capillary column, and Fourier transform-infrared spectroscopy. Geometrical and positional isomerization of linoleic acid occurred during hydrogenation, and many kinds of linoleic acid isomers (trans-9, trans-12; trans-8, cis-12 or cis-9, trans-13; cis-9, trans-12; trans-9, cis-12 and cis-9, cis-12 18:2) were contained in the reaction products. The monoenoic acids in the partial hydrogenation products contained eight kinds of isomers and showed different isomer distributions on Ni, Cu, and Pd catalysts, respectively. The positional isomers of monoenoic acid were produced by double- bond migration during hydrogenation. On Ni and Pd catalysts, the yield of cis-12 and trans-12 monoenoic acids was larger than that of cis-9 and trans-9 monoenoic acids. On the contrary, the yield of cis-9 and trans-9 monoenoic acids was larger than that of cis-12 and trans-12 monoenoic acids on Cu catalyst. From these results, it is concluded that the double bond closer to the methyl group ($\Delta 12$) and that to the carboxyl group $(\Delta 9)$ show different reactivity for hydrogenation on Ni, Cu, and Pd catalysts. Monoenoic acid formation was more selective on Cu catalyst than on Ni and Pd catalysts. JAOCS 73, 1311-1316 (1996).

KEY WORDS: Catalytic hydrogenation, Cu, geometrical and positional isomers, linoleic acid, Ni, Pd, reaction mechanism.

Various vegetable and fish oils, which contain a lot of polyunsaturated fatty acids, exist in the liquid phase at room temperature and atmospheric pressure. The melting point and the resistance to oxidation of oils depend on the amount of unsaturated bonds and on the composition of unsaturated fatty acid isomers in the oils. It is important for the food and surfactant industry to control the melting point and to protect oxidation of the oils by catalytic hydrogenation. Many authors have reported on the catalytic hydrogenation of polyenoic acid methyl esters and natural oils, such as sunflower, rapeseed and soybean oils, with emphasis on reaction kinetics (1–13). Because natural oils contain many kinds of polyunsaturated fatty acids and their isomers, it is too difficult to clarify the reaction mechanism for hydrogenation of natural oils.

In the present study, the catalytic activity and selectivity for the hydrogenation of fatty acids were studied on metal catalysts by employing the hydrogenation of linoleic acid as a model reaction. Recently, analyses of some kinds of dienoic acids and monoenoic acids have been studied in detail by capillary gas-liquid chromatography. Especially, the analyses of octadecadienoic acid isomers and octadecenoic acid isomers have been studied well (14–18). Therefore, the reaction mechanism for the hydrogenation of linoleic acid has been discussed based on the detailed analysis of the reaction products.

EXPERIMENTAL PROCEDURES

Materials. Linoleic acid (Wako Pure Chemical Co. Ltd., Osaka, Japan) contained 96% octadecadienoic acid with both double bonds in the *cis* configuration (*cis*-9,*cis*-12 18:2), 0.3% octadecadienoic fatty acid with two double bonds in the *trans*,*cis* configuration (*trans*-9,*cis*-12 18:2) and 3.5% oleic acid (*cis*-9 18:1). The reactant contained no octadecadienoic fatty acid with both double bonds in the *trans* configuration (*trans*-9,*trans*-12 18:2). Oleic acid (*cis*-9 18:1) was purchased from Kanto Chemicals Co. Ltd. (Tokyo, Japan). Vaccenic acid (*a* mixture of *trans*-11 and *trans*-12 18:1) and elaidic acid (*trans*-9 18:1) were purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan). *Cis*-vaccenic acid (*cis*-12 18:1) was purchased from Sigma Chemical Company (St. Louis, MO).

Catalysts. The precursors of the nickel catalysts were prepared by impregnating silica (Aerosil 380) or alumina (Junsei Pure Chemicals & Co. Ltd., Tokyo, Japan) with an aqueous solution of nickel formate and drying in air at 393K. The nickel content in the precursor was adjusted to be 5 wt% of nickel metal after the decomposition of nickel formate.

The copper catalyst, supported on alumina (Cu/Al_2O_3) and supplied by Nikki Chemicals Co. Ltd. (Tokyo, Japan), contained 41 wt% of Cu. Palladium black was purchased from Nakarai Chemicals Co. Ltd. (Kyoto, Japan).

Procedure. The precursor of the nickel catalyst was placed into a reaction vessel (100 mL) and was calcined *in vacuo* at 573K to decompose nickel formate. Then, the reaction ves-

^{*}To whom correspondence should be addressed at Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi, Niigata, 950-21, Japan.

sel, containing 0.1 g of the resultant catalyst $(Ni/Al_2O_3 \text{ or } Ni/SiO_2 \text{ containing Ni 5 wt\%})$, was cooled to the reaction temperature. Linoleic acid (0.5 g) was immediately introduced into the reaction vessel *in vacuo*, and 300 torr of hydrogen was added to the system. Hydrogenation was carried out in the closed system at 413K.

After the copper (0.1 g of Cu/Al₂O₃ containing Cu 41 wt%) or palladium black (0.1 g) was reduced by H₂ gas of 600 torr at 573K in the reaction vessel, the hydrogenation was performed with the same condition as that described above.

Analysis of the products. The reaction products were converted into methyl esters and analyzed by a gas-liquid chromatograph (Abbreviate GLC, Yanaco GC 3810; Yanagimoto Co., Kyoto, Japan), equipped with Quadrex fused-silica capillary column coated by cyanopropyl methylsilicone (Tokyo Kasei Co. Ltd.).

Separation, identification, and elution order of the reaction products by gas-liquid chromatography (GLC). Figure 1 shows GLC profiles of the fatty acid methyl esters (FAME) of the reaction products obtained by the catalytic hydrogenation of linoleic acid on Ni/SiO₂, Cu/Al₂O₃, and Pd black. The GLC peaks of all octadecadienoic acid geometrical isomers (18:2) are resolved near the base-line (peaks D1 to D5). The D1 peak was assigned to trans-9, trans-12 18:2 by comparing the peak of synthetic trans-9, trans-12 18:2. The elution order of $\Delta 9$, $\Delta 12$ -18:2 geometrical isomers (*trans, trans < cis, trans* < trans, cis < cis, cis) should be used to identify the GLC peaks shown in Figure 1, because this fractionation pattern is identical to the pattern presented in Wolff's paper (19), and the elution order is consistent with the result of Ratnayake and Pelletier (20). Where $\Delta 9$ and $\Delta 12$ represent the position of the double bonds, for example, a double bond between the 9th and 10th carbon atoms from the carboxyl group in linoleic acid is represented by $\Delta 9$ (Ref. Scheme 1). Therefore, the D2 peak is assigned to cis-9, trans-13 or trans-8, cis-12 18:2. The D3, D4 and D5 peaks are respectively assigned to cis-9,trans-12 18:2; trans-9, cis-12 18:2 and cis-9, cis-12 18:2.

Seven resolved peaks (M1-M7 in Fig. 1) were assigned to partial hydrogenation products by the following procedure. Peaks M1, M3, and M7 were respectively assigned to trans-9 18:1; trans-11 18:1 and cis-12 18:1 by the chromatogram of standard samples. Trans-12 18:1 and cis-9 18:1 could not be separated by GLC. It was confirmed that the M4 peak contained both cis-9 18:1 and trans-12 18:1 by using a mixture of the standard samples that contained cis-9 18:1 and trans-12 18:1. Ackman and Hooper (14) reported a similar result that trans-12 18:1 and cis-9 18:1 gave the same retention time on GLC in a flexible fused-silica capillary colomn coated with cyanopropyl phenyl silicone. The M2, M5, and M6 peaks were assigned on the basis of published data (20,21). The M2 peak should be assigned to trans-10 18:1. It can be produced by the double-bond migration from $\Delta 9$ to $\Delta 10$ in the process of partial hydrogenation. The M5 and M6 peaks should be assigned to cis-10 and cis-11 18:1, respectively.

Analysis of trans-12 18:1 and cis-9 18:1. The quantitative analyses of trans-12 18:1 and cis-9 18:1 were performed by the



FIG. 1. Gas chromatograms of the reaction products of the catalytic hydrogenation of linoleic acid on Ni/SiO₂, Pd black, and Cu/Al₂O₃.

infrared (IR) spectroscopic method. The characteristic vibrations of *cis* and *trans* configurations generally appear in the range of $665-730 \text{ cm}^{-1}$ and $960-980 \text{ cm}^{-1}$, respectively. Both linoleic acid (*cis-9,cis-12* 18:2) and oleic acid (*cis-9* 18:1) have characteristic bands at 723 cm⁻¹. On the other hand, the characteristic vibration of elaidic acid (*trans-9* 18:1) was observed at 966 cm⁻¹. The characteristic band of vaccenic acid (a mixture of *trans-11* and *trans-12* 18:1) appeared also at 966 cm⁻¹. Therefore, the quantitative analysis of *trans-12* 18:1 and *cis-9* 18:1 was carried out by using these characteristic bands because the GLC peak of these isomers appeared at the same retention time.



FIG. 2. The intensity ratio of *cis*- to *trans*-octadecenoic acid in Fourier trans form–infrared bands as a function of the concentration ratio of *cis*- to *trans*-octadecenoic acid (18:1). The characteristic vibration bands due to *cis*- and *trans*-unsaturated fatty acids appeared at 723 and 966 cm⁻¹, respectively.

In the range studied here, a linear relationship was obtained between the intensity ratio of the IR band $[I_{723 \text{ cm}}^{-1}/I_{966 \text{ cm}}^{-1}]$ and the molar ratio of $[N_{cis-9 18:1}/N_{trans-9 18:1}]$, as shown in Figure 2, where I and N represent the peak intensities of the characteristic bands and the molar concentration of monoenoic acid, respectively. Here, it is assumed that the C-H bending bands of *cis* configurations in both monoenoic and dienoic acids, such as *cis*-9; *cis*-10; *cis*-11; *cis*-12 18:1; *cis*-9,*cis*-12; *cis*-9,*trans*-12 and *trans*-9,*cis*-12 18:2, which appear at 723 cm⁻¹, have equal adsorption coefficients. A similar assumption is applied to the intensities of the 966 cm⁻¹ peak due to the *trans* configurations in monoenoic and dienoic acids, such as *trans*-9; *trans*-10; *trans*-11; *trans*-12 18:1; *trans*-9,*trans*-12; *trans*-9,*cis*-12 and *cis*-9,*trans*-12 18:2. The total amount (k) of *trans*-12 18:1(x) and *cis*-9 18:1(y) is calculated from GLC analysis (Eq. 1):

$$x + y = k \tag{1}$$

The molar ratio (r) of *cis* component and *trans* component can be expressed as shown in Equation 2.

The amounts of Σ *cis*-isomers and Σ *trans*-isomers except x and y can be obtained from the data of GLC analysis. By using the relationship in Figure 2, r can be estimated from the experi-

mentally determined intensity ratio, $I_{723}^{\text{cm}^{-1}}/I_{966}^{\text{cm}^{-1}}$, of the IR spectrum of the reaction product. The values x and y are determined by solving Equations 1 and 2 and are summarized in Table 1.

RESULTS AND DISCUSSION

Reaction mechanism. The reaction scheme of the catalytic hydrogenation and isomerization of linoleic acid is shown in Scheme 1. It is assumed that the linoleic acid is adsorbed on the surface of the catalyst with one double bond, either $\Delta 9$ or $\Delta 12$. According to the Horiuchi-Polanyi mechanism, the adsorbed linoleic acid is converted to a half-hydrogenated state by the addition of a hydrogen atom (step Ia or Ib)(2,22). The formations of linoleic acid isomers in the products are attributed to a release of a hydrogen atom from the half-hydrogenated species. Geometric isomers are produced by a release of the hydrogen atom from the half-hydrogenated species with a rotation of the C-C bond (IIa or IIf). On the other hand, positional isomers (trans-8, cis-12 or cis-9, trans-13 18:2) were produced by both the abstraction of the hydrogen atom from the adjacent C-H₂ bond of the half-hydrogenated C-C bond and the rotation of the C-C bond during the abstraction of a hydrogen atom (IIc or IId). Further addition of a hydrogen atom to the half-hydrogenated species leads to the production of monoenoic fatty acid isomers (IIb and IIe). For example, when linoleic acid is adsorbed with the $\Delta 9$ in linoleic acid on the active site of the catalyst, not only cis-12 18:1(IIe) and trans-9, cis-12 18:2(IIf) but also trans-8, cis-12 18:2 (IId) is obtained as the product (10).

Hydrogenation and isomerization of the monoenoic acid occur with similar processes. The monoenoic acid (18:1) produced by hydrogenation of linoleic acid in the reaction system is readsorbed and converted to a half-hydrogenated state on the catalyst (IIIa, IIIb). When cis-9 18:1 is readsorbed and in a half-hydrogenated state, an abstraction of the hydrogen atom leads to the production of monoenoic fatty acid isomers, such as cis-10; trans-10 and trans-9 18:1 in the reaction step IVa and IVb. On the other hand, an addition of a hydrogen atom to the half-hydrogenated species leads to the formation of stearic acid. Therefore, the formation of trans-9 18:1 may result from the isomerization of cis-9 18:1 and the hydrogenation of trans-9, trans-12 18:2. The formation of cis-9 18:1 may be attributed to hydrogenation of both cis-9, cis-12 18:2 and cis-9, trans-12 18:2. The positional isomers of 18:1 with double-bond migration, such as trans-10; cis-10; trans-11 and cis-11 are produced by step IVa and IVd, i.e. trans-10 or cis-10 18:1 is formed when a hydrogen atom adds to the 9th car-

$$r = \frac{x + \sum_{i=10}^{12} (cis\ i\ 1\&1) + 2\ (cis\ 9-cis\ 12\ 1\&2) + (cis\ 9-trans\ 12\ 1\&2) + (trans\ 9-cis\ 12\ 1\&2)}{y + \sum_{i=9}^{11} (trans\ i\ 1\&1) + 2\ (trans\ 9-trans\ 12\ 1\&2) + (cis\ 9-trans\ 12\ 1\&2) + (trans\ 9-cis\ 12\ 1\&2)}$$



bon atom in the half-hydrogenated species of the monoenoic acid and the hydrogen atom abstracts from the 11th carbon atom. The *cis*-11 and *trans*-11 18:1 are formed from the species adsorbed with $\Delta 12$ by the similar mechanism as shown in Scheme 1.

Activity and selectivity differences between Ni, Pd, and Cu. The catalytic hydrogenation of linoleic acid was carried out on Ni/SiO₂, Ni/Al₂O₃, Cu/Al₂O₃ and Pd black. The reactions were stopped when a constant amount of hydrogen was consumed in the reaction vessel. The distribution of the reaction products is summarized in Table 1. The hydrogenation activity on Cu catalyst was much lower than on Ni and Pd catalysts. The difference in catalytic activity of the metal catalysts is attributed to the ability to adsorb hydrogen because the hydrogen adsorption ability of Cu is lower than that of Ni and Pd (23). Earlier studies (2,4,10–13) have reported that hydrogenation of polyunsaturated fatty acid esters can be described by a first-order consecutive reaction. The hydrogenation of linoleic acid can be described by the consecutive reactions (10): octadecadienoic acid (18:2) \rightarrow octadecenoic acid (18:1) \rightarrow stearic acid (18:0).

Stearic acid. As shown in Table 1, only a small amount of stearic acid is produced in the catalytic hydrogenation of linoleic acid on Cu/Al_2O_3 . On the other hand, a considerable amount of stearic acid is produced on Ni/SiO_2 , Ni/Al_2O_3 , and Pd catalysts. This difference apparently can be attributed to the difference in adsorption abilities of monoenoic acids on the metal catalysts. The adsorption ability of monoenoic acid on Cu is lower than that on Ni and Pd. Therefore, a considerable amount of stearic acid is formed by the readsorption of some part of monoenoic acid is monoenoic acid on Ni and Pd catalysts.

Monoenoic acids. Distributions and ratios of *trans/cis* in the partial hydrogenation products are summarized in Table 2. Eight geometric and positional isomers of octadecenoic acid (18:1) are contained in the products. The octadecenoic acid (18:1) in the products obtained on the different catalysts had different isomer compositions. On Ni/SiO₂, Ni/Al₂O₃,

TABLE 1	
Fatty Acid Composition in the Reaction Products of the Catalytic Hydrogenat	ion of Linoleic Acid on Metal Catalyst

				Products distribution (mol%)				
		Reaction	Reactant	Ni/SiO ₂ ^b	Ni/Al ₂ O ₃ ^b	Cu/Al ₂ O ₃ ^b	Pd black ^b	
		time	(mol%)	Ni = 5 mg	Ni = 5 mg	Cu = 41 mg	Pd = 100 mg	
Peak number ^a	Fatty acid	(min)	0	70	105	1480	98	
S	18:0			2.3	2.9	0.3	1.8	
M1	trans-9 18:1			1.5	1.7	7.2	3.7	
M2	trans-10 18:1			4.1	3.2	5.5	6.0	
M3	trans-11 18:1		0.2	3.6	3.1	6.7	6.1	
M4	trans-12 + cis-9 18:1		3.3 ^d	11.8	12.3	9.4	8.8	
	(trans-12 18:1) ^c			(7.8)	(7.7)	(1.5)	(8.8)	
	(cis-9 18:1) ^c			(4.0)	(4.6)	(7.9)	(trace)	
M5	<i>cis</i> -10 18:1			1.3	1.1	2.4	2.0	
M6	<i>cis</i> -11 18:1			1.1	1.1	2.1	1.7	
M7	<i>cis</i> -12 18:1			5.3	7.3	1.4	2.9	
D1	trans-9, trans-12 18:2			trace	trace	trace	0.4	
D2	trans-8, cis-12 + cis-9, trans-13 18:2			2.4	2.2	0.9	1.5	
D3	cis-9, trans-12 18:2			trace	trace	1.5	0.2	
D4	trans-9, cis-12 18:2		0.3	2.6	2.5	1.2	3.0	
D5	cis-9, cis-12 18:2		96.3	64.0	62.6	46.4	60.7	
К	Unknown ^e			trace	trace	15.0	1.2	
Selectivity for stearic acid ^f				6.9	8.1	0.8	5.2	
Degree of hydrogenation ^g				33.3	35.6	35.3	34.8	

^aPeak numbers correspond with Figure 1.

^b100 mg of the catalyst was used. The weight in the column shows the metal weight contained in the catalyst.

^cQuantitative analysis of *cis*-9 18:1 and *trans*-12 18:1 was carried out by IR spectroscopy.

^dIt was confirmed by infrared (IR) spectroscopy that peak number M4 in the reactant contained only *cis*-9 18:1 as an impurity.

^ePeak K gave a large retention time and was observed in only the hydrogenation product catalyzed by Cu/Al₂O₃.

^fSelectivity for stearic acid is calculated by the equation: [(stearic acid)/(degree of hydrogenation)] imes 100.

^{*g*}Degree of hydrogenation = $\Sigma[(18:1) + 2(18:0)]$.

and Pd, the yields of *trans*-12 18:1 and *cis*-12 18:1 are larger than those of *trans*-9 18:1 and *cis*-9 18:1, respectively. On Cu/Al_2O_3 , on the contrary, the yields of *trans*-9 18:1 and *cis*-9 18:1 are larger than those of *trans*-12 18:1 and *cis*-12 18:1, respectively.

These results suggest that a double bond closer to the carboxyl group ($\Delta 9$) shows greater reactivity than one closer to the methyl end of the chain ($\Delta 12$) on the Ni/SiO₂, Ni/Al₂O₃, and Pd catalysts. On the contrary, with the Cu/Al₂O₃ catalyst, a double bond closer to the methyl end of the chain ($\Delta 12$) is more reactive than one closer to the carboxyl group ($\Delta 9$).

As shown in Table 2, the molar ratios of *trans* 18:1 to *cis* 18:1 in the hydrogenation product on the Ni and Cu catalysts were 1.1–1.5. On Pd catalyst, the ratio was 3.7 and was larger than that on the other catalysts. In general, Pd formed more *trans* isomers than Ni (24).

Dienoic acids. The distribution of dienoic acid isomers in the products were different on Ni, Pd, and Cu catalysts, as shown in Table 1. With the Ni/SiO₂ and Ni/Al₂O₃ catalysts, *trans*-8,*cis*-12(or *cis*-9,*trans*-13) and *trans*-9,*cis*-12 18:2 were observed in the product, although the formations of *cis*-9,*trans*-12 and *trans*-9,*trans*-12 18:2 were negligibly small. As shown in Scheme 1, *cis*-12 18:1; *trans*-9,*cis*-12 and *trans*-8,*cis*-12 18:2 would be produced *via* the species adsorbed with Δ 9 on the catalyst. Assuming that most of the D2 peak in the products formed on the Ni/SiO₂ and Ni/Al₂O₃ catalysts is due to *trans*-8,*cis*-12 18:2 [although that is assigned to the overlap of *trans*-8,*cis*-12 and *cis*-9,*trans*-13 18:2 by Ratnayake and Belletier (20)], we can interpret the distribution of dienoic acid isomers in the products on the basis of the reaction mechanisms **IId** and **IIf** in Scheme 1. The reason why *trans*-9,*trans*-12 and *cis*-9,*trans*-12 18:2 were negligibly small may be due to less reactivity of Δ 12 on Ni catalysts. This belief is supported by the difference in reactivity between Δ 9 and Δ 12, as mentioned in the section on the formation of monoenoic acid isomers.

On the Cu catalyst, the amount of positional isomers of 18:2 (trans-8,cis-12 or cis-9,trans-13 18:2) was smaller than on the Ni catalysts. This means that migration of the double bond occurs with difficulty on the Cu catalyst. Cis-9, trans-12 18:2 was produced on the Cu catalyst, while on Ni catalyst, it was not found in the reaction products. In the reaction on Cu/Al₂O₃, the Δ 12 double bond exhibited high reactivities to both partial hydrogenation and cis/trans isomerization. Assuming that the adsorption of dienoic acid (18:2) is stronger than that of monoenoic acid, both cis/trans isomerization of dienoic acid and partial hydrogenation would be promoted, and formation of stearic acid from monoenoic acid isomers would therefore be inhibited. On Cu/Al₂O₃, the concentration of cis-9, trans-12 18:2 is slightly larger than trans-9, cis-12 18:2. This indicates also that the reactivity of $\Delta 12$ is higher than that of $\Delta 9$ (IIa in Scheme 1). Unknown materials that

TABLE 2		
Distribution of Octadecenoic Acid Isomers (18:1) Produced by	Catalytic Hydrogenation of Linoleic Ac	id

	Distribution of octadecenoic acid isomers (mol%)										
Catalyst	trans-9	trans-10	trans-11	trans-12	cis-9	<i>cis</i> -10	<i>cis-</i> 11	cis-12	Σtrans	Σcis	Σtrans/Σcis
Cu/Al ₂ O ₃	7.2	5.5	6.7	1.5	7.9	2.4	2.1	1.4	20.9	13.8	1.5
Ni/SiÔ	1.5	4.1	3.6	7.8	4.0	1.3	1.1	5.3	17.0	11.7	1.5
Ni/Al ₂ Ô ₂	1.7	3.2	3.1	7.7	4.6	1.1	1.1	7.3	15.7	14.1	1.1
Pd Black	3.7	6.0	6.1	8.8	trace	2.0	1.7	2.9	24.6	6.6	3.7

gave large retention times in the gas chromatogram were found in only the products reacted on the Cu/Al_2O_3 catalyst. Analysis of the unknown materials is now in progress.

With Pd as the catalyst, the amount of *trans*-9,*cis*-12 18:2 was double that of *cis*-9,*trans*-12 18:2. This result indicates that the species adsorbed with $\Delta 9$ in linoleic acid is more abundant than the species adsorbed with $\Delta 12$ in linoleic acid on Pd catalyst. Because *trans*-12 18:1 and *cis*-12 18:1 are formed by hydrogenation of $\Delta 9$ in linoleic acid and *trans*-9,*cis*-12 18:2 is formed by isomerization of $\Delta 9$ in linoleic acid during hydrogenation, they are the most abundant in the partially hydrogenated product.

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