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Catalytic Hydrogenation of Linoleic Acid over Platinum-Group Metals Supported on Alumina

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ABSTRACT: Catalytic activity and selectivity for hydrogenation of linoleic acid (*cis*-9,*cis*-12 18:2) were studied on Pt, Pd, Ru, and Ir supported on Al_2O_3. Stearic acid (18:0) and 10 different octadecenoic isomers (18:1) in the products could be separated completely by using a new capillary column coated by isocyanopropyl trisilphenylene siloxane for gas–liquid chromatography. The monoenoic acid isomers and dienoic acid isomers in the products on the various catalysts showed different distributions. The catalysts exhibited nearly equal selectivity for stearic acid formation. The 12-position double bond in linoleic acid has higher reactivity than the 9-position double bond in catalytic hydrogenation on platinum-group metal catalysts. In addition to hydrogenation products of linoleic acid, geometrical and positional dienoic acid isomers (*trans*-9,*trans*-12; *trans*-8,*cis*-12; *cis*-9,*trans*-13; *trans*-9,*cis*-13; *cis*-9,*trans*-12 18:2), due to isomerization of linoleic acid during hydrogenation, were contained in the reaction products. Ru/Al_2O_3 exhibited the highest activity for isomerization of linoleic acid with the noble metal catalysts. Conjugated octadecadienoic acid isomers have been observed in products of the reaction on Pt/Al_2O_3, Ru/Al_2O_3, and Ir/Al_2O_3. Catalytic activities of noble metals for positional and geometric isomerization of linoleic acid during hydrogenation decreased in the sequence of Ru $\geq$ Pt $>$ Ir $\gg$ Pd.

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KEY WORDS: Catalytic hydrogenation, *cis/trans* isomerization, double-bond migration, isomers of dienoic and monoenoic acids, iridium, linoleic acid, palladium, platinum, ruthenium, selectivity for monoenoic acid.

In a previous report (1), the catalytic activity and selectivity for hydrogenation of linoleic acid were studied on Cu, Ni, and Pd. The distributions of geometrical and positional isomers were analyzed in detail to clarify the reaction mechanism for catalytic hydrogenation of polyunsaturated fatty acids. Geometrical and positional isomerization of linoleic acid occurred during the hydrogenation because many kinds of isomers of dienoic acid and partial hydrogenation products were contained in the reaction products. Distribution of the isomers of dienoic acids and monoenoic acids in the reaction products varied with the catalyst.

The catalytic hydrogenation of oils and fatty acids on noble metal catalysts has been investigated by many authors (2–6). Catalytic properties of these metals, such as selectivities for stearic acid formation, and activity were studied. However, the activity for *cis-trans* isomerization and double-bond migration during hydrogenation of fatty acids were studied separately with small olefins as model reactants because detailed analysis of monoenoic and dienoic acids had been impossible. Ackman and Hooper (7) have reported on detailed analysis of C_{18} fatty acid isomers by gas–liquid chromatography (GLC). Since then, many researchers have reported on the analysis of fatty acid isomers by using GLC equipped with capillary columns (8–10). The catalytic activity and selectivity for the hydrogenation of linoleic acid were studied on noble metal catalysts. From the distributions of isomers of the monoenoic and dienoic acids in the reaction products, the characteristics of the noble metal catalysts were discussed.

EXPERIMENTAL PROCEDURES

Materials. Linoleic acid (Wako Pure Chemical Co. Ltd., Osaka, Japan) was used as the reactant. Its composition was *cis*-9,*cis*-12 18:2 = 94.6%; *trans*-9,*cis*-12 18:2 = 0.4%; *cis*-9, *trans*-12 18:2 = 0.4%; *cis*-9 18:1 = 3.9%; cis-11 18:1 = 0.3%, and conjugated 18:2 isomers = 0.4%.

Catalysts. The precursor of the Ir catalyst was prepared by impregnating alumina with an aqueous solution of iridium chloride and drying *in vacuo* at room temperature. It was oxidized at 873 K. The iridium content in the precursor was adjusted to 5 wt% of iridium metal. Platinum supported on Al_2O_3 was prepared as follows: $H_2PtCl_6{\cdot}6H_2O$ (Hayashi Pure Chem. Ind. Ltd., Osaka, Japan) was impregnated onto Al_2O_3 (Merck Type T, Merck, Darmstadt, Germany) and was reduced by formalin in KOH aqueous solution. The Pt content was adjusted to 5%.

The Pd and Ru catalysts supported on alumina (Pd/Al_2O_3 and Ru/Al_2O_3) were prepared and supplied by Nikki Chemicals Co. Ltd. (Tokyo, Japan).

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Procedure. Each catalyst (0.1 g) was placed into a reaction vessel (100 mL) and was reduced by hydrogen gas at 443 K. After reduction of the catalyst, the reaction vessel was evacuated at 443 K for 1 h and cooled to the reaction temperature (413 K). Linoleic acid (0.5 g) was immediately introduced into the reaction vessel *in vacuo,* and 300 torr of hydrogen gas was added to the system. Hydrogenation was carried out in the closed system at 413 K.

Analysis of the products. The reaction products were converted into methyl esters and analyzed by a gas–liquid chromatograph (GLC) (GC-14B; Shimadzu Co. Ltd., Tokyo, Japan), equipped with a capillary column coated by isocyanopropyl trisilphenylene siloxane (registered trademark is TC-70; GL Science Co. Ltd., Tokyo, Japan). Ten peaks due to octadecenoic acid isomers, five peaks due to octadecadienoic acid isomers, and six or seven peaks due to unknown materials were observed in the GLC profile of the product. Ten peaks due to octadecenoic acid isomers and five peaks due to octadecadienoic acid isomers were assigned by using standard samples. Details of analysis will be published in the future. GLC–mass spectroscopy (GC–MS) analysis was performed with a QP-5000 mass spectrometer and a GC-17A GLC (Shimadzu Co. Ltd., Kyoto, Japan). The ^{1}H nuclear magnetic resonance (NMR) spectra of products were measured at 500 MHz with a Varian UNITY plus-500NB Fourier transform–NMR spectrometer (Palo Alto, CA).

RESULTS AND DISCUSSION

Two double bonds exist in linoleic acid. One is located between the ninth and tenth carbon atom from the carboxyl end (abbreviated as $\Delta 9$), and the other is found between the twelfth and thirteenth carbon atom (abbreviated as $\Delta 12$).

Catalytic hydrogenation of linoleic acid was carried out on Pt/Al$_2$O$_3$, Pd/Al$_2$O$_3$, Ru/Al$_2$O$_3$, and Ir/Al$_2$O$_3$. The reactions were stopped when a constant amount of hydrogen had been consumed in the reaction vessel. The distributions of the reaction products are summarized in Table 1. The products produced on different metal catalysts showed different distributions of both octadecadienoic acid isomers (18:2) and octadecenoic acid isomers (18:1).

Identification of unknown peaks in GLC. In the previous paper (1), we reported that unknown materials were detected by GLC in the product made with Cu catalyst. In these experiments on Pt, Ru, and Ir catalysts, significant amounts of unknown materials were also detected by GLC. Six or seven peaks due to unknown material were found beyond the peak for linoleic acid. Their retention times and peak patterns were

TABLE 1
Fatty Acid Composition (mol%) in the Reaction Products of the Catalytic Hydrogenation of Linoleic Acid on Metal Catalysts

			Products distribution (mol%); reaction time (min)			
Sample designation	Fatty acid	Reactant (mol%)[a]	Pt/Al$_2$O$_3$[b] (Pt = 5 mg) (146)	Ru/Al$_2$O$_3$ (Ru = 5 mg) (96)	Ir/Al$_2$O$_3$ (Ir = 5 mg) (128)	Pd/Al$_2$O$_3$ (Pd = 5 mg) (7)
S	18:0		6.8	6.1	5.7	7.4
M1	*trans*-9 18:1		3.6	3.4	2.3	3.3
M2	*trans*-10 18:1		2.2	3.3	2.4	3.8
M3	*trans*-11 18:1		2.3	3.0	2.3	4.0
M4	*trans*-12 18:1		1.8	1.9	1.3	1.7
M5	*trans*-13 18:1		1.5	1.3	1.1	1.5
M6	*cis*-9 18:1	3.9	4.9	6.6	6.9	7.4
M7	*cis*-10 18:1		1.2	1.0	1.0	1.0
M8	*cis*-11 18:1	0.3	1.1	1.2	1.0	1.1
M9	*cis*-12 18:1		2.0	3.4	2.9	3.6
M10	*cis*-13 18:1		0.6	0.4	0.4	0.4
D1	*trans*-9,*trans*-12 18:2		1.4	3.0	1.8	0.6
D2	*trans*-8,*cis*-12 + *cis*-9,*trans*-13 18:2		4.0	3.0	2.3	1.2
D3	*cis*-9,*trans*-12 18:2	0.4	4.0	7.2	4.6	1.7
D4	*trans*-9,*cis*-12 18:2	0.4	4.2	6.3	4.3	1.6
D5	*cis*-9,*cis*-12 18:2	94.6	50.0	40.1	53.6	59.0
K[c]	Conjugated dienoic acid	0.4	8.5	8.5	6.3	0.3
	Selectivity for stearic acid[d]		19.5	16.2	17.3	17.4
	Degree of hydrogenation[e]		34.8	37.7	33.0	42.6

[a] Reaction time, 0 min.

[b] Catalyst in the amount of 100 mg was used. The weight listed in the column is the amount of metal contained in the catalyst.

[c] Peak K gave a large retention time.

[d] Selectivity for stearic acid is calculated by the equation: [(stearic acid)/(degree of hydrogenation)] × 100.

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

the same as those obtained on Cu catalyst (1). Mass numbers of the unknown materials were measured by GC–MS. In GC–MS analysis, only a peak at m/e = 294, due to $C_{17}H_{31}COOCH_3$, was observed as a parent peak in mass spectra for each of the unknown peaks in the GLC. Because the amount of hydrogen consumed in the reaction agreed with the amount of hydrogen necessary to produce both monoenoic acid and stearic acid in the product, the unknown material in the product should be assigned to octadecadienoic acid isomers (18:2).

The ^{1}H-^{1}H homonuclear shift correlation spectroscopy (COSY NMR spectrum) of the products indicated the presence of dienoic acid (18:2) with two conjugated double bonds, and the double bonds could exist in the range from the fifth to the thirteenth carbon atom from the carboxyl end. The double bond located between the fifteenth and sixteenth carbon atom from the carboxyl end (Δ15) was not observed in NMR (Kitayama, Y., M. Takahashi, and M. Okamura, unpublished data), although Wolff, Nour, and Bayard (11) reported that the elution order of *cis*-12,*trans*-15 18:2; *cis*-9,*trans*-15 18:2; *trans*-12,*cis*-15 18:2; and *cis*-12,*cis*-15 18:2 isomers in GLC analysis was after linoleic acid and before the trienoic acid isomers. Therefore, most of the unknown materials obtained in this experiment have been assigned to dienoic acid isomers with conjugated double bonds, such as *cis*-10,*trans*-12 18:2; *cis*-10,*cis*-12 18:2; *trans*-10,*cis*-12 18:2; *trans*-10,*trans*-12 18:2; *cis*-9,*cis*-11 18:2; *cis*-9,*trans*-11 18:2; *trans*-9,*cis*-11; and *trans*-9,*trans*-11 18:2, produced by double-bond migration in linoleic acid during the hydrogenation process. A detailed report of the ^{1}H-^{1}H COSY NMR data of the isomers of octadecenoic and octadecadienoic acids will be presented later.

Distribution of dienoic acid isomers. Distributions of *trans* isomers in dienoic acids of the products are summarized in Table 2. A large amount of dienoic acid isomers was found in the products from Ru and Ir catalysts. Total amounts of *trans* dienoic acid isomers, except conjugated dienoic acid isomers, in the reaction products on Ru/Al_2O_3, Pt/Al_2O_3, and Ir/Al_2O_3 catalysts (5 wt% metal content) were 2–3 times larger than those on Pd/Al_2O_3. Formation of *trans* dienoic acid isomers, except conjugated dienoic acid isomers, at a similar degree of hydrogenation on the catalysts (5 wt% metal content) decreased in the order Ru/Al_2O_3 > Pt/Al_2O_3 ≥ Ir/Al_2O_3 ≫ Ni/Al_2O_3* > Pd/Al_2O_3 > Cu/Al_2O_3* (*see Ref. 1).

The amount of *trans*-9,*cis*-12 18:2 was nearly equal to that of *cis*-9,*trans*-12 18:2 on the platinum-group catalysts. The results indicate that the reactivity for *cis/trans* isomerization of the Δ9 double bond in linoleic acid is similar to that of the Δ12 double bond, although the reactivity for hydrogenation is larger for Δ12 than for Δ9.

With Ni/Al_2O_3 and Cu/Al_2O_3 as catalysts, octadecadienoic fatty acid with both double bonds in the *trans* configuration (*trans*-9,*trans*-12 18:2) was rarely observed in the products (1). However, with Ru, Pt, and Ir catalysts, considerable amounts of *trans*-9,*trans*-12 18:2 were obtained in the products.

Distribution of monoenoic acid isomer. Ten geometrical and positional isomers of octadecenoic acid (18:1) were contained in the products. Neither *cis*-8 18:1 nor *trans*-8 18:1 was observed in the products, but *cis*-13 18:1 and *trans*-13 18:1 were observed. This means that the double bond does not migrate to the carboxyl end but rather to the methyl end. The distribution and molar ratio of *cis/trans* in the partial hydrogenation products of linoleic acid are summarized in Table 3. The *cis/trans* ratio of monoenoic acids produced on the different metal catalysts is presented in the sequence Ir/Al_2O_3 ≫ Ru/Al_2O_3 > Pt/Al_2O_3 = Pd/Al_2O_3. The order is different from the order, Pt > Ir > Ru > Rh > Pd, given by Zajcew (12) and Reisz *et al.* (13) for hydrogenation of tall oil and soybean oil.

As shown in Table 3, the double bonds closer to the methyl group (Δ12) and to the carboxyl group (Δ9) in linoleic acid have different reactivities. In the partial hydrogenation of linoleic acid, Δ12 was more reactive than Δ9 on the noble metal catalysts.

Selectivity for monoenoic acid formation. Linoleic acid converts to stearic acid *via* monoenoic acid isomers consecutively. As shown in Table 1, platinum-group catalysts exhibited nearly equal selectivity for monoenoic formation at substantially the same degree of hydrogenation (about 35%). The selectivities for monoenoic acid formation on the platinum-group metal catalysts were 60–68%. With Cu/Al_2O_3 catalyst, the selectivity for monoenoic acid formation was 97.9% as shown in Table 3 (1). Hydrogenation activities of these catalysts at the same wt% of metal decreased in the order of Pd ≫

TABLE 2
Distribution of Dienoic Acid Isomers (18:2) in the Products Produced During Catalytic Hydrogenation of Linoleic Acid

	Products distribution (mol%)						
Catalyst	*t*-9,*t*-12[a]	*t*-8,*c*-12 + *c*-9,*t*-13	*c*-9,*t*-12	*t*-9,*c*-12	Conjugated 18:2	Total (unconjugated)	Total
Ni/Al_2O_3	0.4	2.1	2.1	2.2	trace	6.8	6.8
Cu/Al_2O_3	trace	1.8	1.0	1.0	15.4	3.8	19.2
Pd/Al_2O_3	0.6	1.2	1.7	1.6	0.3	5.1	5.4
Pt/Al_2O_3	1.4	4.0	4.0	4.2	8.5	13.6	22.1
Ru/Al_2O_3	3.0	3.0	7.2	6.3	8.5	19.5	28.0
Ir/Al_2O_3	2.9	2.2	4.1	3.6	6.3	12.8	19.1

[a] *t* = *trans*; *c* = *cis*.

TABLE 3
Distribution of Stearic Acid (18:0) and Monoenoic Acid (18:1) Isomers Produced by Catalytic Hydrogenation of Linoleic Acid

	Product distribution (mol%)													
Catalysts	St[a]	*t*-9[b]	*t*-10	*t*-11	*t*-12	*t*-13	*c*-9	*c*-10	*c*-11	*c*-12	*c*-13	Selectivity[c]	$\Sigma\Delta9/\Sigma\Delta12$	$\Sigma\Delta c/\Sigma\Delta t$
Ni/Al_2O_3	3.5	2.2	3.7	3.7	1.3	0.9	12.5	0.6	1.0	8.0	trace	82.9	1.6	1.9
Cu/Al_2O_3	0.4	9.7	3.8	3.5	3.2	3.4	7.9	1.8	1.7	1.6	0.6	97.9	3.7	0.6
Pd/Al_2O_3	7.4	3.3	3.8	4.0	1.7	1.5	7.4	1.0	1.1	3.6	0.4	65.3	2.0	0.9
Pt/Al_2O_3	6.8	3.6	2.2	2.3	1.8	1.5	4.9	1.2	1.1	2.0	0.6	60.9	2.2	0.9
Ru/Al_2O_3	6.1	3.4	3.3	3.0	1.9	1.3	6.6	1.0	1.2	3.4	0.4	67.6	1.9	1.0
Ir/Al_2O_3	5.7	2.3	2.4	2.3	1.3	1.1	6.9	1.0	1.0	2.9	0.4	65.5	2.2	1.3

[a]St: Stearic acid. [b]*t* = *trans*; *c* = *cis*. [c]Selectivity = [(the sum of monoenoic acid isomers)/(degree of hydrogenation)] × 100.

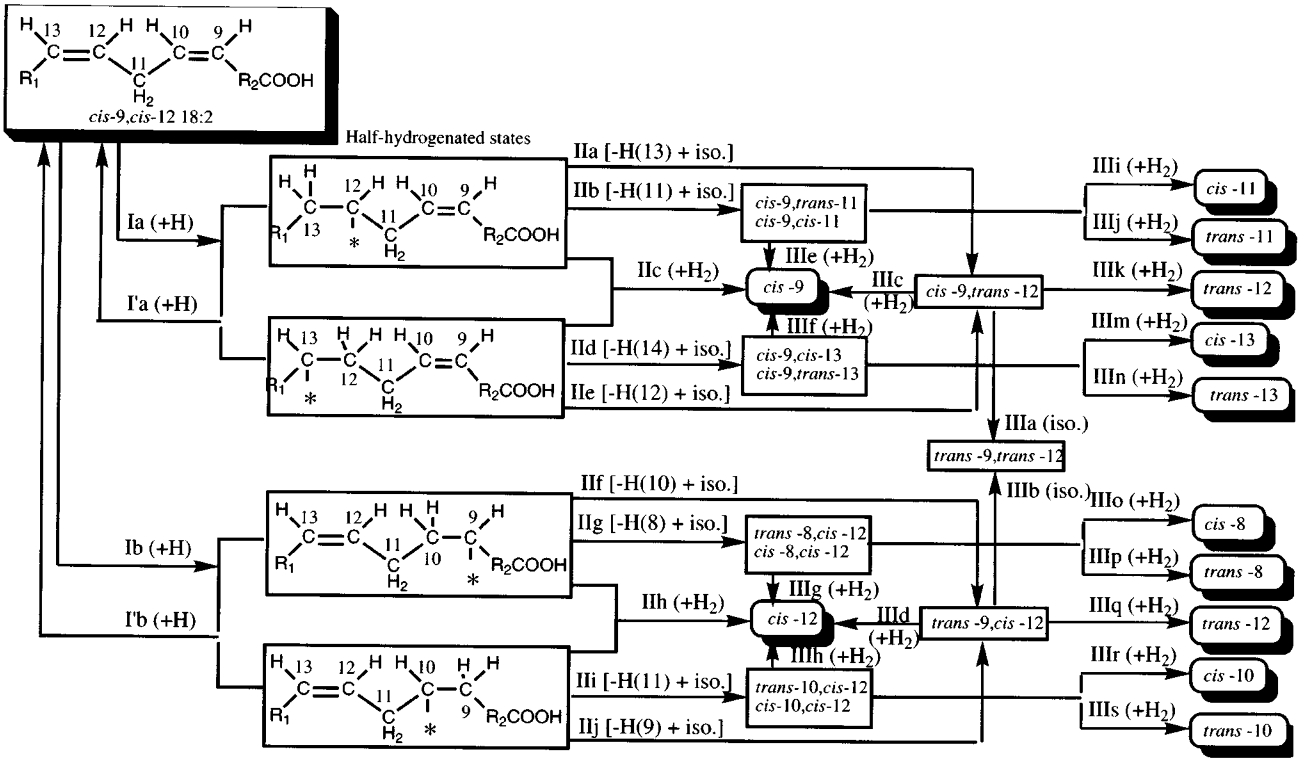
Ru > Ir ≥ Pt > Ni > Cu. From these results, selectivity for monoenoic acid formation has no relation to catalytic activity. The selectivity for monoenoic acid formation is apparently attributable to the difference in adsorption ability between monoenoic acid and dienoic acid on metal catalysts. When the adsorption ability of dienoic acid is stronger than that of monoenoic acid, the formation of monoenoic acid should have priority to that of stearic acid in the hydrogenation process.

Reaction mechanism. Previously, we reported that catalytic hydrogenation of linoleic acid takes place *via* the half-hydrogenated state on metal catalysts (1):

$$\text{dienoic acid} \rightleftarrows \text{half-hydrogenated state} \rightarrow \text{monoenoic acid} \rightarrow \text{stearic acid} \quad [1]$$

If we suppose that the conversion of a half-hydrogenated species of linoleic acid to monoenoic acid is a rate-determining step, the adsorbed linoleic acid should attain a pre-equilibrium state with the half-hydrogenated state.

Isomerization of linoleic acid. Scheme 1 shows a reaction mechanism for partial hydrogenation and isomerization of linoleic acid. As shown, the formation of linoleic acid isomers (18:2) in the products is attributable to the release of a hydrogen atom from the half-hydrogenated species (II a, b, d, e, f, g, i, and j). Geometric isomers are produced by the release of the hydrogen atom from the half-hydrogenated species with rotation of the C-C bond (step II a, e, f, and j). On the other hand, the unconjugated dienoic acid isomers, such as *cis*-8,*cis*-12 18:2; *cis*-8,*trans*-12 18:2; *cis*-9,*cis*-13 18:2; and *cis*-9,*trans*-13 18:2, were produced by release of the



SCHEME 1

hydrogen atom from the adjacent $-CH_2$ bond (eighth or fourteenth carbon atom) of the half-hydrogenated C–C bond and rotation of the C–C bond during the abstraction of the hydrogen atom (II d or II g).

Conjugated dienoic isomers, such as *cis*-9,*cis*-11 18:2; *cis*-9,*trans*-11 18:2; *cis*-10,*cis*-12 18:2; and *trans*-10,*cis*-12 18:2, are produced by the abstraction of a hydrogen atom from the eleventh $-CH_2-$ (between two ethylenic bonds) in the half-hydrogenated state of linoleic acid (II b and II i).

Further addition of a hydrogen atom to the half-hydrogenated species leads to the production of monoenoic acid isomers (II c and II h) (14).

It has been reported that the double bond in oleic acid migrates toward the methyl end during hydrogenation on Ni and Pd catalysts under special conditions (15).

It is interesting that *trans*-9,*trans*-12 18:2 was rarely found in the products obtained over Ni, Cu, and Pd. On the other hand, a significant amount of *trans*-9,*trans*-12 18:2 was found in products produced over Ru/Al_2O_3, Ir/Al_2O_3, and Pt/Al_2O_3. This may be caused by a stronger adsorption of linoleic acid on Ru, Ir, and Pt than on the other catalysts.

Monoenoic acid formation. Diagrams of the formation of monoenoic acid isomers are shown in Scheme 1. The *cis*-monoenoic acid isomers are produced by the following processes: (i) partial hydrogenation of linoleic acid itself (II c, II h); (ii) in the first step, isomerization of linoleic acid leads to *cis,trans* 18:2 or *trans,cis* 18:2, and then partial hydrogenation of the *trans* double bond in *cis,trans* 18:2 or *trans,cis* 18:2 isomers takes place (III c, d, e, f, g, h, i, m, o, and r).

On the other hand, *trans*-monoenoic acid isomers are produced by the following processes: (i) isomerization of *cis*-9 18:1 or *cis*-12 18:1 produced by the hydrogenation of linoleic acid; (ii) partial hydrogenation of the *cis* double bond in *cis,trans* or *trans,cis* dienoic acid isomers as shown in Scheme 1 (III j, k, n, p, q, and s).

From the scheme, 12 species of octadecenoic acid isomers can exist in the reaction product. However, only 10 species of octadecenoic acid isomers were obtained in our experiment. The isomers *trans*-8 18:1 and *cis*-8 18:1 were not found in the products, although *trans*-13 18:1 and *cis*-13 18:1 were observed. The results show that the double bond in linoleic acid does not migrate to the carboxyl end but to the methyl end during hydrogenation.

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