Deodorization of Vegetable Oils. Part I: Modelling the Geometrical Isomerization of Polyunsaturated Fatty Acids

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ABSTRACT: Laboratory-scale treatments of canola oils similar to deodorization were carried out by applying the following conditions: reduced pressure with nitrogen or steam stripping at different temperatures ranging from 210 to 270°C for 2–65 h. The formation of the group of *trans* linolenic acid isomers follows a first-order reaction and the kinetic constant varies according to the Arrhenius' law. Similar results were observed for the *trans* isomerization of linoleic acid. Based on these experiments, a mathematical model was developed to describe the isomerization reaction steps occurring in linoleic and linolenic acids during deodorization. The calculated degrees of isomerization are independent of the composition of the oil but related to both time and temperature of deodorization. The degree of isomerization of linolenic acid is unaffected by the decrease of this acid content observed during the deodorization. Deodorization at about 220–230°C appears to be a critical limit beyond which the linolenic isomerization increases very strongly. The newly established model can be a tool for manufacturers to reduce the total *trans* isomer content of refined oils, and was applied to produce a special selectively isomerized oil for a European Nutritional Project.

Paper no. J8867 in *JAOCS 76*, 73–81 (January 1999).

KEY WORDS: Deodorization, isomerization, kinetics, linoleic acid, linolenic acid, modelling, *trans* isomer fatty acids.

The present work is a part of a study carried out within the framework of a European contract entitled "Nutritional and Health Impact of *trans* Polyunsaturated Fatty Acids in European Populations." The aim of this project was to assess the metabolic effects of the *trans* linolenic acid isomers in the human diet.

Two special qualities of fully refined low erucic rapeseed oil (canola oil) were required in this study: (i) a canola oil containing no *trans* isomers of oleic, linoleic, and linolenic acids; (ii) a selectively isomerized canola oil enriched in *trans* linolenic acid isomers (5%) but without or with the possible minimum level of *trans* oleic and linoleic acid isomers (a ratio of 10 between the *trans* linolenic acid and the *trans* linoleic acid contents was the accepted limit).

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As early as 1973 Ackman showed that during deodorization, geometrical isomerization of linoleic and linolenic acids occurs, even under regular industry conditions (1). According to Wolff (2,3), *trans* isomers of linoleic acid account for 0.2–1.0% of total fatty acids while *trans* isomers of linolenic acid may add up to 3% in commercial soybean and canola oils. Residence time and operating temperature of deodorization have the most important effects on the extent of *trans* isomer formation (4). Kinetic measurements concerning geometrical isomerization of linolenic acid showed that the reaction is a first-order one and that the isomerization constant varies with temperature according to Arrhenius' law (5,6).

Apart from the fact that the probability of linolenic acid isomerization is considered to be 12–14 times higher than that of linoleic acid (7), no scientific study comparing the kinetics of isomerization of linoleic and linolenic acids during deodorization has been published. Thus, in order to produce the particular isomerized oil needed for the projected nutritional study, it was decided to develop a mathematical model to predict the operating conditions for the selective isomerization. The present paper discusses the established model in detail as well as its relation to the above-mentioned project.

EXPERIMENTAL PROCEDURES

Materials. Canola oils, including one deodorized oil, and a refined sunflower oil for laboratory experiments were supplied by the Cereol refinery located in Coudekerque-Branche (France). A refined linseed oil was supplied by Robbe Company (Compiègne, France). The fatty acid compositions of the oils are given in Table 1. The starting bleached canola oils contained no measurable amounts of *trans* isomers of oleic and linoleic acids and only very small amounts of *trans* linolenic acid isomers (0.05–0.06%). The deodorized canola oil contained no *trans* isomers of oleic acid, a small quantity of *trans* linoleic acid isomers, and a larger amount of *trans* linolenic acid isomers.

Laboratory-scale deodorizations. In this paper, the term deodorization will be used to mean isomerizing deodorization, not to be confused with the regular steam-vacuum deodorization operations usually part of edible oil refining. The deodor-

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TABLE 1
Fatty Acid Composition (%) of the Oils Used for the Tests

	Canola oil no.							
	1[a]	2[a]	3[a]	4[a]	5[a]	7[b]	Sunflower oil[b]	Linseed oil[b]
Experiment no.	4–5	1	2	3	6-8	7		
C_{16}	4.8	5.1	4.9	4.9	4.9	4.8	6.1	5.4
C_{18}	1.9	1.7	1.8	1.8	1.8	1.8	4.0	4.0
$C_{18:1}$	59.3	58.4	60.0	60.2	60.1	59.9	23.7	21.3
cis $C_{18:2}$	21.5	21.1	20.5	20.4	20.4	20.8	63.7	14.5
trans $C_{18:2}$	—	—	—	—	0.1	0.4	<0.1	
cis $C_{18:3}$	8.4	9.65	8.54	8.44	8.55	7.24	0.1	54.8
trans $C_{18:3}$	—	0.05	0.06	0.06	0.05	1.26	—	0.2

[a]Bleached oils.
[b]Deodorized oils.

izations were carried out under reduced pressure using a homemade deodorizer with a total capacity of 3.2 L. The stripping gas, steam or nitrogen, was injected into the oil through small holes arranged in the sparger plate at the bottom of the deodorizer. The oil was introduced into the equipment under vacuum and heated by means of an external electric jacket. About 20 min was needed to reach a final temperature of 200°C . The overheating before the temperature could be stabilized was less than 10°C and lasted no longer than 10 min. The operating temperature was kept to within ±1°C. In order to avoid water condensation inside the deodorizer, nitrogen gas stripping was always used below 120°C at the beginning and at the end of the operation. The pressure in the equipment during deodorization was less than 3 mm Hg absolute.

The residence time was started when the deodorization temperature was reached. When a long-term experiment was interrupted (discontinuous operation), the oil was cooled at the end of the day and stored in the deodorizer under a positive nitrogen pressure until the next deodorization step. In this way, a lengthy deodorization time was the cumulative deodorization time of several steps. After the deodorization was completed, the oil was cooled with cold water flowing through a coil located inside the deodorizer. Sampling for analysis was carried out by applying a nitrogen overpressure inside the deodorizer before opening the bottom valve. The hot sample was then quickly cooled and stored in a tightly closed vial until analysis.

Fatty acid analysis. Fatty acid methyl esters (FAME) were prepared according to the following method: 0.5 mL of a methanolic 0.5 M NaOH solution was added to 20 to 30 mg of the oil in a screw-cap glass tube. The mixture was heated for at least 5 min at a temperature of 70°C. After cooling, 0.5 mL of a boron trifluoride/methanol complex solution was added (solution 20% in methanol—Merck Schuchard, Hohenbrunn, Germany). The tube was heated again under the same conditions. FAME were extracted twice with 2 mL of *n*-heptane after diluting the methanolic solution with saturated brine.

In order to avoid the risk of overlap of the methyl esters of some mono-*trans* isomers of linolenic and gadoleic acids (20:1), and also for the best stability of the columns, *trans* fatty acids were determined using two different capillary columns instead of the CP-SIL88 column (Chrompack, Middleburg, The Netherlands) more widely used. A BPX70 (70% cyanopropyl polysilphenylene-siloxane) fused-silica capillary column 60 m × 0.32 mm i.d., 0.25 µm film thickness [SGE, Villeneuve St. Georges, France] was used to separate the *trans* linoleic acid isomers from the original *cis* one (Fig. 1). Helium was used as the carrier gas at a flow rate of 1.9 mL/min. The sample was analyzed on a Carlo Erba 4100 gas chromatograph (Carlo Erba Strumentazione, Milano, Italy). The injector was heated to 270°C and the flame-ionization detector to 280°C. The oven temperature was held at 160°C for 40 min, then increased to 220°C at 8°C/min followed by a 5 min hold. The largest *trans* linoleic acid isomers (*c* = *cis* and *t* = *trans*) were eluted at 28.6 min (*c,t*) and 29.2 min (*t,c*), while the original linoleic acid (*c,c*) was eluted at 29.9 min (8). The small degree of isomerization of the linoleic acid required in the project allowed us to omit the minor di-*trans* isomer possibly overlapped at about 27.2 min by a nonidentified peak. An HP-FFAP (cross-linked polyethylene glycol-TPA) fused capillary column 25 m × 0.2 mm i.d., 0.33 µm film thickness (Hewlett-Packard, Les Ulis, France) was used for the determination of the *trans* linolenic acid isomer content (Fig. 2). Hydrogen was the carrier gas at a flow rate of 1.2 mL/min. The samples were analyzed on an HP-5890 Series II gas chromatograph (Hewlett-Packard, Palo Alto, CA). The injector was heated to 300°C and the flame-ionization detector to 250°C. The oven temperature was increased first from 170 to 190°C at 1°C/min, then to 220°C at 2°C/min followed by a 14 min hold. The *trans* isomers were located by comparing the chromatograms of the methyl esters of an isomerized and a nonisomerized canola oil. The individual *trans* isomers were named by taking into account their quantitative distribution (2–5) and their order of elution on the polar capillary columns. The main *trans* isomers were eluted at 18.8 min (*c,c,t* and *t,c,t*), 19.3 min (*c,t,c*), and 19.6 min (*t,c,c*). The original linolenic acid (*c,c,c*) was eluted at 19.0 min. The *t,t,c* and *c,t,t* isomers were minor isomers not detected here (5).

Because of small quantitative differences existing between the two columns, the final fatty acid composition for expressing the result as area% was achieved by using the FFAP column; the *cis* and *trans* isomer contents of linoleic acid were

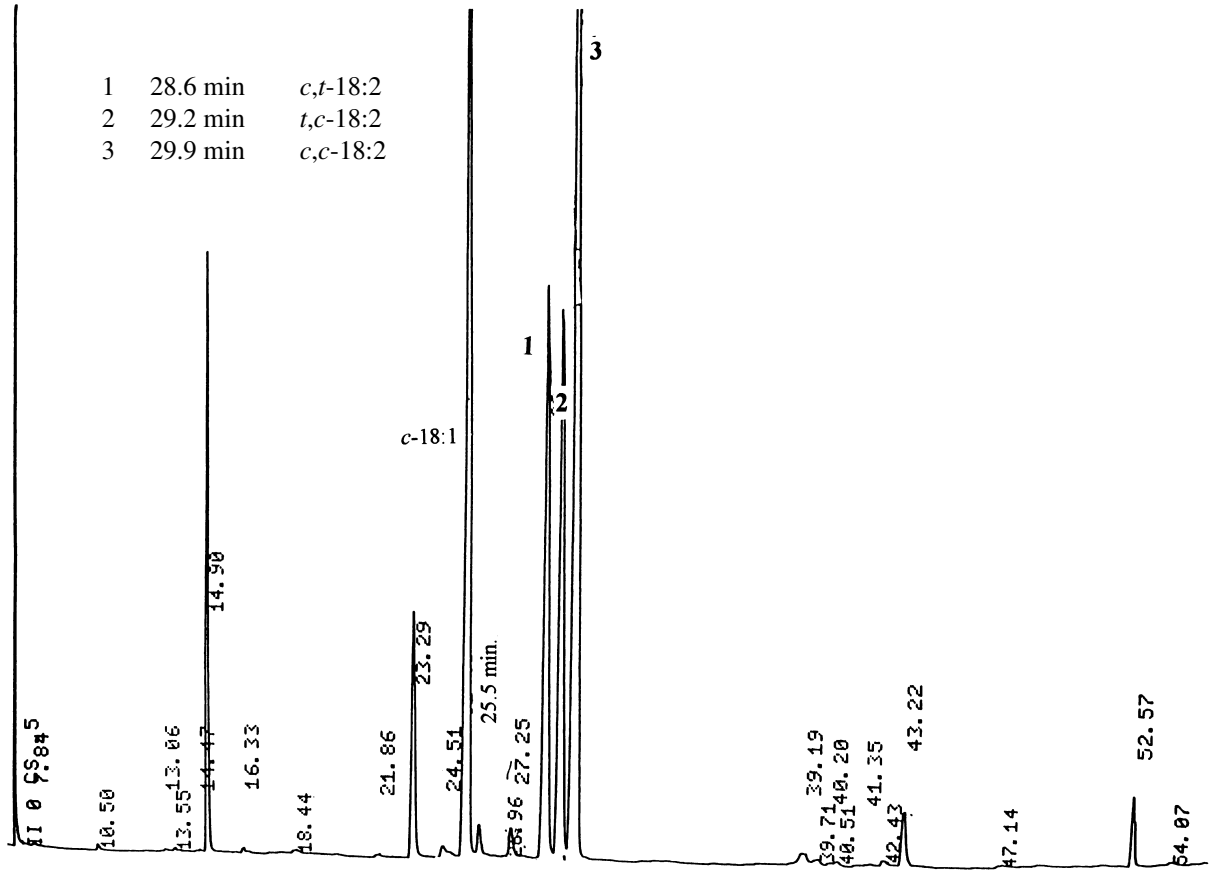

FIG. 1. Fatty acid methyl esters of an isomerized sunflower oil. BPX70 capillary column, 60 m × 0.32 mm, 0.25 µm film; 160°C (hold 40 min) to 220°C at 8°C/min (hold 5 min).

recalculated according to their proportions determined on the BPX70 column. The total *trans* linoleic or linolenic acid isomer content is the sum of the concentrations of the individual *trans* isomers separated on each of the columns.

The gas chromatography equipment was calibrated using a FAME mixture (Alltech Templeuve, France) containing 20% of each of the following FAME: $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$.

Microsoft Excel version 95 (Redmond, WA) was used for all calculations.

RESULTS

Deodorization tests were carried out on canola oils at temperatures ranging from 210 to 270°C over 2 to 65 h (Table 2). All the trials were conducted with nitrogen or steam stripping in a discontinuous way, except for experiment 3, although it lasted a long time (48 h), and experiments 6 and 8, which lasted no longer than 6 h.

The level of isomerization of the polyunsaturated fatty acids of the oils sampled at different times for each deodorization are expressed by their *cis* linoleic (*cis L*) and *cis* linolenic (*cis Ln*) fractions (Table 3). The *cis* linoleic acid isomer fraction of a sample at time *t* is the ratio between its *cis* linoleic acid isomer content (*cis* $C_{18:2}$) and its total linoleic acid content (tot $C_{18:2}$).Total linoleic acid content means the sum of the *cis* and *trans* isomer contents. In the same way, the *cis* linolenic acid isomer fraction of this sample is the ratio between its *cis* linolenic acid isomer content (*cis* $C_{18:3}$) and its total linolenic acid content (tot $C_{18:3}$). Values at time 0 concern the oils before heating, except for experiment 8, in which a sample was taken just when the deodorization temperature of 270°C was reached; for this sample, the fact that *cis L* and *cis Ln* were less than 1 at time 0 proves that isomerization had

TABLE 2
Operating Conditions Used for the Canola Oil Deodorizations

Experiment (no.)	Temperature (°C)	Total time (h)	Stripping gas	Operating mode
1	210	65	Nitrogen	Discontinuous
2	220	47.3	Steam	Discontinuous
3	220	48	Nitrogen	Continuous
4	235	12	Steam	Discontinuous
5	235	12	Nitrogen	Discontinuous
6	250	6	Steam	Continuous
7	250	11	Steam	Discontinuous
8	270	2	Steam	Continuous

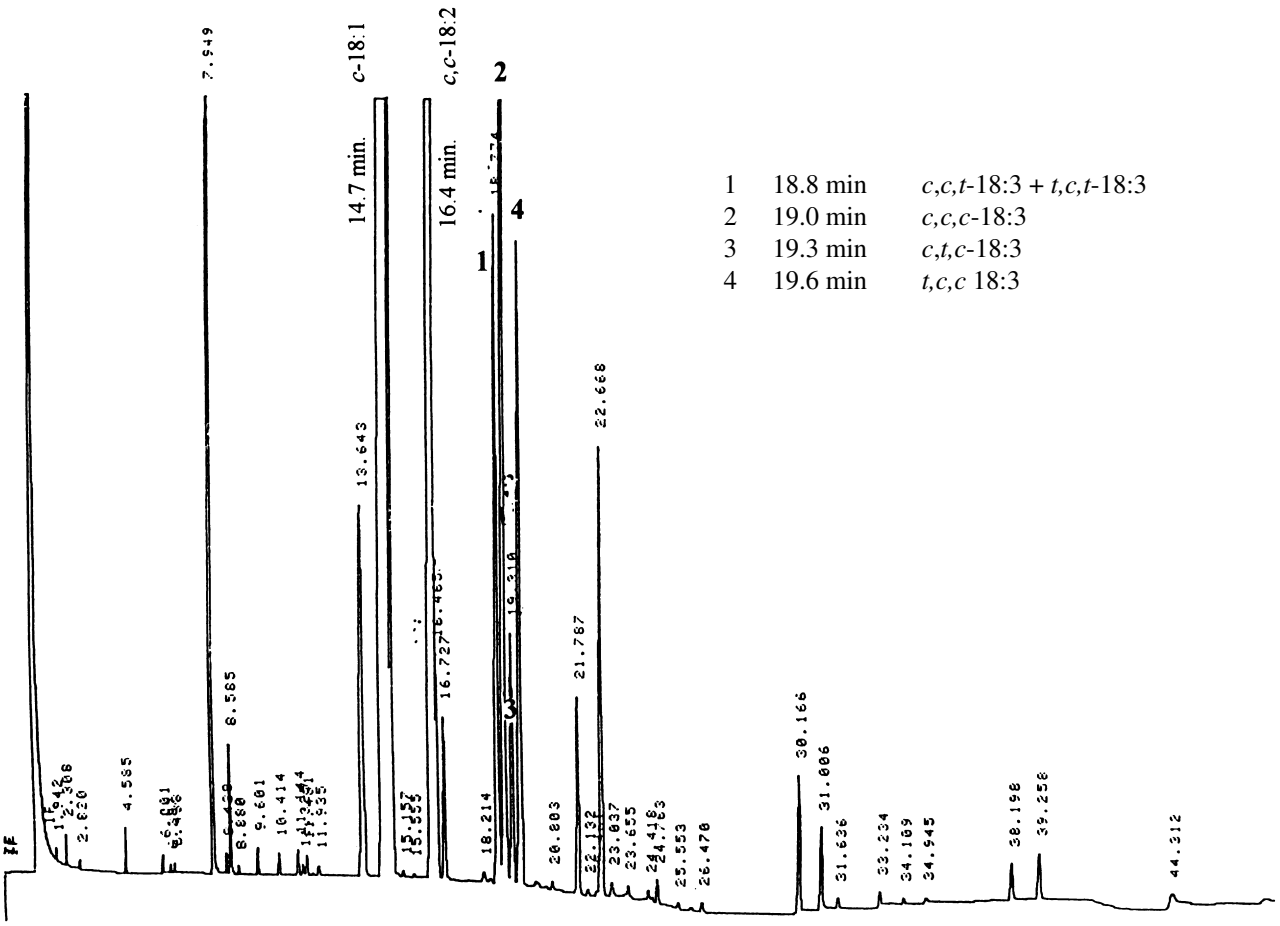

FIG. 2. Fatty acid methyl esters of an isomerized canola oil. FFAP capillary column (Hewlett-Packard, Les Ulis, France), 25 m × 0.32 mm, 0.33 µm film; 170 to 190°C at 1°C/min, then to 200°C at 2°C/min (hold 14 min).

already occurred during the heating time. This is also probable at lower temperatures but to a much lesser extent. In experiment 7, the initial ratios (*cis L* and *cis Ln*) are lower than 1, due to the fact that a fully refined oil was used for the test.

The logarithm of the *cis* linolenic acid isomer fraction as a function of the deodorization time produced linear relationships for each trial (Table 4: only 2 points for experiment 3). The linear relationships confirmed that the isomerization of linolenic acid is a first-order reaction. Identical conclusions are deduced from the equivalent curves drawn for linoleic acid (Table 4).

The absolute values of the slopes of the different straight lines measure the isomerization constants of linoleic and linolenic acids, $K_{(L)}$ and $K_{(Ln)}$ respectively (Table 4). These constants are about 10% higher than those published by Wolff (3).

The fact that the *y*-intercepts of the curves are not zero may be partly due to the inaccuracies of the measurements, but are more likely due to the fact that the deodorization time was counted after the heating period, during which some isomerization occurred. For experiment 7, the use of a deodorized oil had no significant effect on the isomerization constant but resulted in an increase of the *y*-intercept.

For both linoleic and linolenic acids, the isomerization constants followed Arrhenius' law: the logarithm of the isomerization constant is a linear function of the reciprocal of the absolute temperature T ($R^2 = 1.00$).

Linoleic acid : $\log K_{(L)} = -7921.95/T + 12.76$

Linolenic acid: $\log K_{(Ln)} = -6796.63/T + 11.78$

In order to obtain a more accurate model for the deodorization step of the oil refining, the linolenic acid loss occurring during the deodorization—probably caused by its degradation—has to be taken into account. The equations used to describe the decrease of the linolenic acid content during the deodorization have been determined previously (9). No significant loss was observed for linoleic acid.

Isomerization of linoleic acid.

$$\Rightarrow \log(cis\ C_{18:2})_t = -K_{(L)} \cdot t + \log(\text{tot } C_{18:2})_{t=0} \quad [1]$$

TABLE 3
***cis* Isomer Fractions of the Canola Oils Sampled During the Deodorizations**

Experiment (no.)	Temperature (°C)	Time (h)	*cis L*[a]	*cis Ln*[b]	Experiment (no.)	Temperature (°C)	Time (h)	*cisL*[a]	*cisLn*[b]
1	210	0	1.000	0.948	6	250	0	1.000	0.994
		33.5	0.982	0.632			2	0.984	0.695
		58	0.969	0.472			3	0.975	0.601
		65	0.963	0.434			4	0.961	0.509
							5	0.951	0.496
2	220	0	1.000	0.993			6	0.945	0.399
		10	0.995	0.794					
		20	0.984	0.653	7	250	0	0.993	0.851
		30	0.972	0.516			2	0.974	0.628
		39.7	0.964	0.425			3	0.965	0.547
		47.3	0.952	0.364			4	0.957	0.479
							5	0.950	0.416
3	220	0	1.000	0.993			6	0.939	0.371
		48	0.952	0.354			7	0.927	0.312
							8	0.920	0.275
4	235	0	1.000	1.000			9	0.910	0.251
		2	0.994	0.872			10	0.904	0.231
		3	0.992	0.822			11	0.896	0.210
		4	0.988	0.772					
		5	0.986	0.731	8	270	0[c]	0.995	0.943
		6	0.982	0.691			0.17	0.991	0.853
		9	0.973	0.579			0.33	0.984	0.773
		11	0.966	0.525			0.5	0.979	0.719
		12	0.962	0.493			0.67	0.970	0.672
							0.83	0.971	0.622
5	235	0	1.000	1.000			1	0.961	0.581
		8	0.973	0.630			1.25	0.954	0.523
		9	0.970	0.606			1.5	0.946	0.474
		10	0.967	0.562			1.75	0.940	0.422
		11	0.963	0.535			2	0.926	0.392
		12	0.957	0.507					

[a]*cis* Linoleic acid isomer fraction.
[b]*cis* Linolenic isomer fraction.
[c]Sampling at the operating temperature.

equation equivalent to: $(cis\ C_{18:2})_t = (\text{tot}\ C_{18:2})_{t=0} \cdot 10^{-K(L)\cdot t}$

$$\Rightarrow \log K_{(L)} = -7921.95/T + 12.76 \text{ or } K_{(L)} = 10^{[-7921.95/T + 12.76]} \quad [2]$$

$$\Rightarrow (trans\ C_{18:2})_t = (\text{tot}\ C_{18:2})_{t=0} \cdot (1 - 10^{-K(L)\cdot t}) \quad [3]$$

Degradation of linolenic acid ($k_{d(Ln)}$ in h^{-1} is the degradation constant of linolenic acid).

$$\Rightarrow \log(\text{tot}\ C_{18:3})_t = -k_{d(Ln)}\cdot t + \log(\text{tot}\ C_{18:3})_{t=0} \quad [4]$$

equation equivalent to: $(\text{tot}\ C_{18:3})_t = (\text{tot}\ C_{18:3})_{t=0} \cdot 10^{-kd(Ln)\cdot t}$

$$\Rightarrow (\log k_{d(Ln)} = -7503.3/T + 12.12 \text{ or } k_{d(Ln)} = 10^{[-7503.3/T + 12.12]} \quad [5]$$

Isomerization of linolenic acid.

$$\Rightarrow \log(cis\ C_{18:3})_t = -K_{(Ln)}\cdot t + \log(\text{tot}\ C_{18:3})_t \quad [6]$$

equation equivalent to: $(cis\ C_{18:3})_t = (\text{tot}\ C_{18:3})_t \cdot 10^{-K(Ln)\cdot t} = (\text{tot}\ C_{18:3})_{t=0} \cdot 10^{-[K(Ln) + k_d(Ln)]\cdot t}$

$$\Rightarrow (trans\ C_{18:3})_t = (\text{tot}\ C_{18:3})_{t=0} \cdot 10^{-kd(Ln)\cdot t}\,(1 - 10^{-K(Ln)\cdot t}) \quad [7]$$

$$\Rightarrow \log K_{(Ln)} = -6796.63/T + 11.78 \text{ or } K_{(Ln)} = 10^{[-6796.63/T + 11.78]} \quad [8]$$

where:
$(\text{tot}\ C_{18:2})_{t=0}$ = initial linoleic acid content of the oil,
$(cis\ C_{18:2})_t$ = *cis* linoleic acid isomer content at time *t*,
$(\text{tot}\ C_{18:3})_{t=0}$ = initial linolenic acid content of the oil,
$(\text{tot}\ C_{18:3})_t$ = total linolenic acid content of the oil at time *t*,
$(cis\ C_{18:3})_t$ = *cis* linolenic acid isomer content of the oil at time *t*, and $(trans\ C_{18:2})_t$ and $(trans\ C_{18:3})_t$ equal, respectively, *trans* linoleic and *trans* linolenic acid isomer concentrations formed at time *t* in the oil.

Interesting practical conclusions can be drawn from this model in order to get a better understanding of the isomerization during deodorization.

Degree of isomerization (DI). DI is usually expressed as a percentage by the ratio between the *trans* linoleic acid (or linolenic acid) isomer content and the corresponding total linoleic acid (or linolenic acid) content. Those ratios can be easily calculated using the following equations:

Linoleic acid: $(cis\ C_{18:2})_t/(\text{tot}\ C_{18:2})_t = 10^{-K(L)\cdot t}$

$$DI_L\ (\%) = 100\,(1 - 10^{-K(L)\cdot t}) \quad [9]$$

TABLE 4
Isomerization Constants (h^{-1}) of Linoleic $K_{(L)}$ and Linolenic $K_{(Ln)}$ Acids

		Linoleic acid			Linolenic acid		
Experiment (no.)	Temperature (°C)	R^2 values	$K_{(L)}$	*y* intercept	R^2 values	$K_{(Ln)}$	*y* intercept
1	210	0.996	2.5×10^{-4}	+0.0002	0.999	55.3×10^{-4}	–0.0060
2	220	0.986	4.5×10^{-4}	+0.0012	0.999	92.3×10^{-4}	–0.0049
3	220	1.000	4.5×10^{-4}	0	1.000	93.4×10^{-4}	–0.0031
4	235	0.996	14.0×10^{-4}	+0.0004	0.998	251.4×10^{-4}	–0.0079
5	235	0.994	15.3×10^{-4}	+0.0002	0.999	246.6×10^{-4}	–0.0003
6	250	0.991	43.2×10^{-4}	+0.0007	0.979	631.3×10^{-4}	–0.0193
7	250	0.998	41.2×10^{-4}	–0.0030	0.993	557.6×10^{-4}	–0.0927
8	270	0.991	150.1×10^{-4}	–0.0018	0.996	1886.6×10^{-4}	–0.0424

Linolenic acid: $(cis\ C_{18:3})_t/(\text{tot}\ C_{18:3})_t = 10^{-K(Ln)\cdot t}$

$$DI_{Ln}\ (\%) = 100\ (1 - 10^{-K(Ln)\cdot t}) \qquad [10]$$

The first important conclusion, since the reactions studied are of first order, is that the degrees of isomerization of linoleic and linolenic acids are independent of the initial content of these fatty acids. They depend only on the deodorization temperature and time. In the case of linolenic acid, the degree of isomerization is also unaffected by the degradation of this fatty acid.

Curves representing the degrees of isomerization of linolenic and linoleic acids as a function of the time of deodorization at different temperatures are drawn in Figures 3 and 4, respectively. At low temperatures, a very long deodorization is needed to observe a significant level of isomerization of linolenic acid. Below 210°C for linolenic acid and 250°C for linoleic acid, the degrees of isomerization appear to be approximately linear as a function of time. A deodorization temperature of 220–230°C seems to be a critical point above which linolenic acid isomerization increases very strongly. The critical temperature is higher for linoleic acid, over 240°C. At 270°C, 80% of the linolenic acid is isomerized in 4 h while the degree of isomerization of linoleic acid stays at a low level of about 13% (Fig. 5).

Within the conditions applied in most industrial processing, i.e., less than 4 h at a temperature lower than 240°C, the calculated degrees of isomerization of linolenic acid are less than 30%, which is in fact the upper limit value observed in commercial European refined oils (2). Higher values, up to 37%, were measured by O'Keefe in oils purchased in the U.S. retail market (11).

Selectivity S *of the isomerization.* The selectivity *S* of the isomerization of the linolenic acid vs. the linoleic acid can be defined by the ratio $K_{(Ln)}/K_{(L)}$ between the isomerization constants of these two acids. Using the equations [8] and [2] , *S* is expressed by the relation:

$$S = 10^{-6796.63/T + 11.78}/10^{-7921.95/T + 12.76}$$

$$S = 10^{1125/T - 0.98}$$

or

$$\log S = 1125/T - 0.98$$

The selectivity *S* only depends on the temperature of the deodorization; it decreases to one-third of its value at 180°C when the temperature rises to 280°C (Table 5).

The selectivity defined above is different from the relative probability of formation of the linolenic and linoleic geometrical isomers proposed by Wolff (5,7) as the ratio between the degrees of isomerization of linolenic and linoleic acids.

One of the stated constraints in the European project mentioned was to have the lowest possible *trans* linoleic acid isomer content combined with the targeted 5% *trans* linolenic acid isomer content. This requires a high selectivity and, therefore, a deodorization at a low temperature.

Impact of the linolenic acid degradation on the trans *content.* The *trans* linolenic acid isomer content of a deodorized oil is the result of a competition between the isomerization of

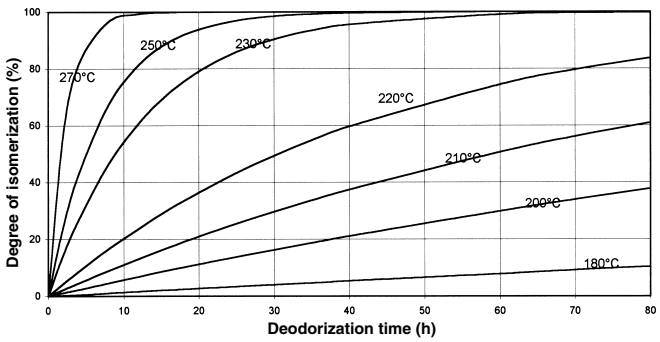

FIG. 3. Degree of isomerization of linolenic acid as a function of time.

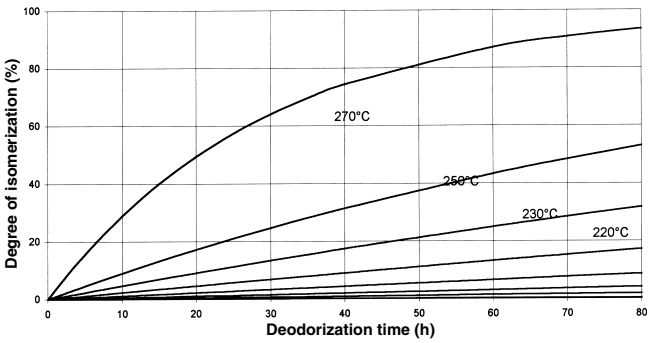

FIG. 4. Degree of isomerization of linoleic acid as a function of time.

TABLE 5
Selectivity *S* of the *trans* Isomerization of $C_{18:3}$ vs. $C_{18:2}$ at Different Deodorization Temperatures

Temperature (°C)	*S*	Temperature (°C)	*S*
180	32	260	14
200	25	270	12
220	20	280	11
240	16		

linolenic acid and the loss of this acid. Therefore, for a given oil, the maximum *trans* linolenic acid isomer content that can be obtained during deodorization is less than the initial linolenic acid content. The maximum *trans* linolenic acid isomer content of two oils with very different linolenic acid contents (canola and linseed oils) is shown by the curves drawn in Figures 6 and 7. The time t_{max} required to reach that maximum value can be calculated using the equations of the model:

$$t_{max} = -[1/K_{(Ln)}] \cdot \log[k_{d(Ln)}/(k_{d(Ln)} + K_{(Ln)})]$$

At that time, the first derivative with respect to *t* in Equation 7 relative to the *trans* linolenic acid isomer content is equal to zero.

This reaction time needed to obtain the maximum *trans* linolenic acid isomer content depends only on the temperature and is independent of the initial linolenic acid content of the oil. It decreases by approximately half for each 10°C increase in temperature (Table 6). The maximum *trans* content varies and is evident from the initial linolenic acid content, but relatively small changes are observed with temperature (Table 7).

Due to the absence of loss of linoleic acid during deodorization, the total *trans* linoleic acid isomer content always increases with time.

Deodorization time t. The time *t* during which a certain amount of *trans* linolenic acid isomers is formed at a given temperature can be calculated as follows:

$$t = [1/(k_{d(Ln)} + K_{(Ln)})] \cdot \log\{(C_{18:3})_{t=0}/[(C_{18:3})_{t=0} \cdot 10^{-kd(Ln)\cdot t} - (trans\ C_{18:3})t]\}$$

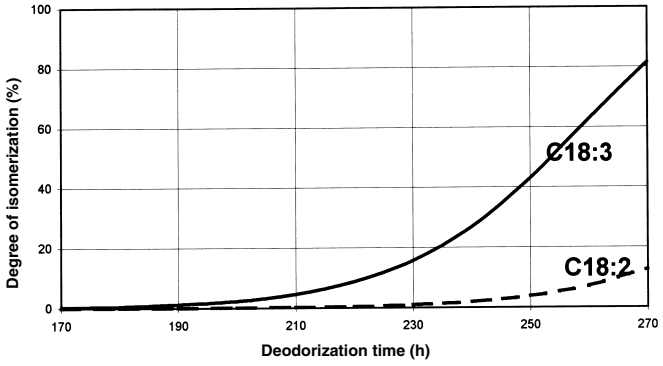

FIG. 5. Degrees of isomerization of linoleic and linolenic acids for a 4 h deodorization as a function of the temperature.

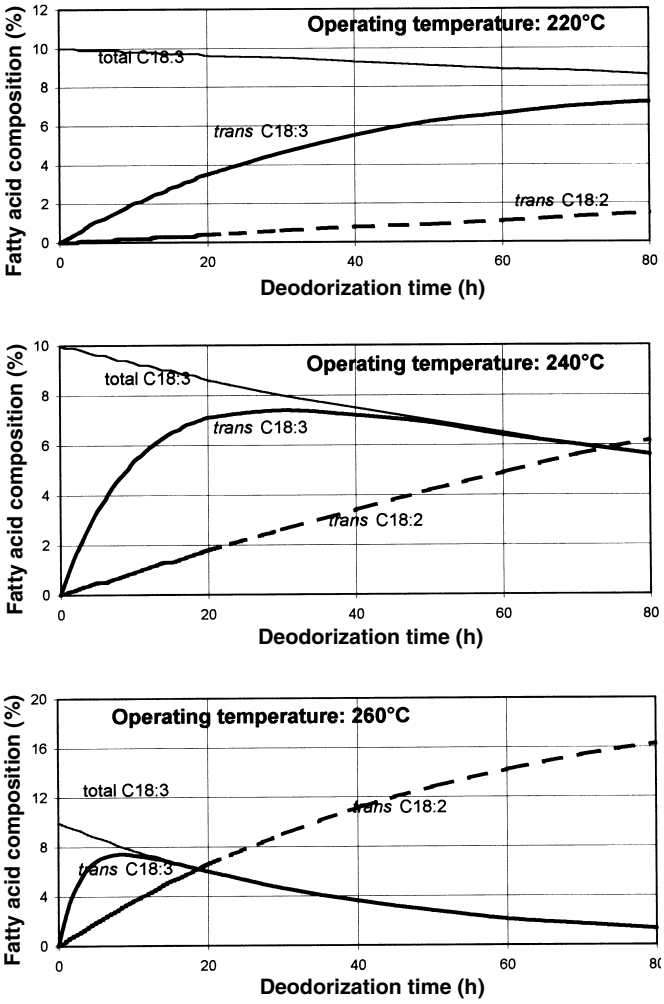

FIG. 6. Canola oil: effect of linolenic acid losses on *trans* isomerization.

To resolve this equation, an iterative procedure has to be applied until the value of *t* calculated in the first member of the equation is equal to the value of *t* supposed in the second member of the equation.

Calculations of the time necessary to form 5% of *trans* linolenic acid isomers have been completed for temperatures from 170 to 270°C for a bleached canola oil with an initial total linolenic acid content of 10% and a total linoleic acid content of 21%. The results plotted in Figure 8 show a dramatic increase in the deodorization time with the decrease in-

TABLE 6
Time (t_{max}) Needed to Reach the Maximum *trans* Linolenic Acid Isomer Content

Temperature (°C)	t_{max} (h)	Temperature (°C)	t_{max} (h)
180	2538	230	69
190	1162	240	36
200	550	250	20
210	268	260	11
220	134	270	6

TABLE 7
Maximum *trans* Linolenic Acid Isomer Content Formed at t_{max} for Two Different Oils

	Canola oil ($C_{18:3}$ = 9%)		Linseed oil ($C_{18:3}$ = 55%)	
Temperature (°C)	*trans* (%)	*cis* (%)	*trans* (%)	*cis* (%)
180	7.07	0.22	43.2	1.35
200	6.88	0.27	42.1	1.68
220	6.70	0.33	41.0	2.04
240	6.53	0.40	39.9	2.44
260	6.36	0.47	38.8	2.87
270	6.27	0.51	38.3	3.10

temperature. The relationship between the logarithm of time and temperature is close to linear.

Ratio R *between* trans *linolenic acid isomer and* trans *linoleic acid isomer content. R* can be expressed by the relation:

$$R = F(t) \cdot (C_{18:3})_{t=0}/(C_{18:2})_{t=0}$$

with $F(t) = 10^{-kd(Ln)\cdot t} \cdot (1 - 10^{-K(Ln)\cdot t})/(1 - 10^{-K(L)\cdot t})$.

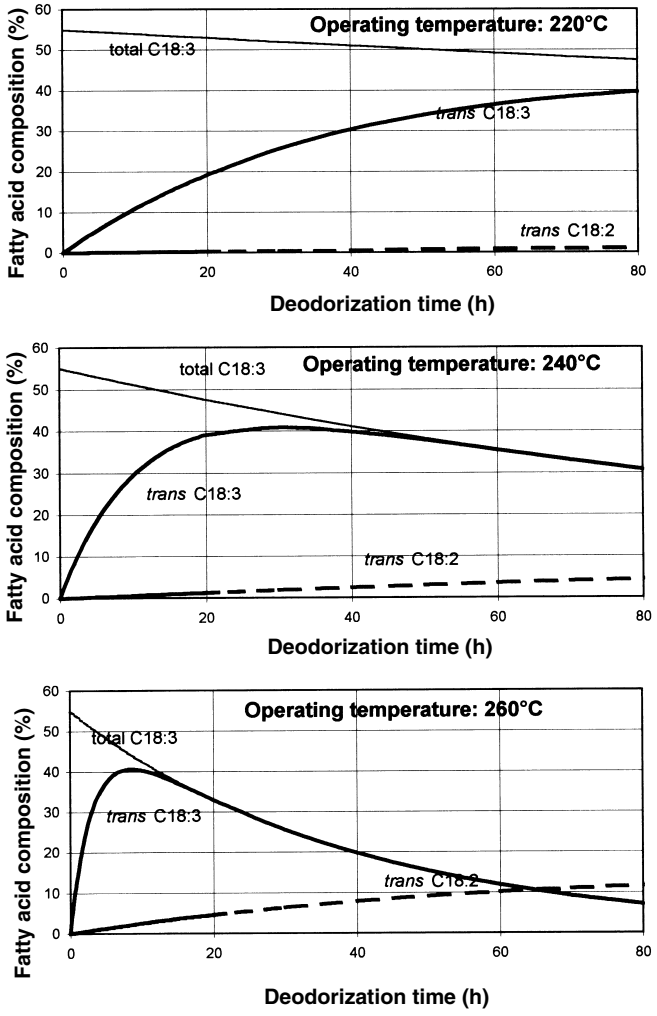

FIG. 7. Linseed oil: effect of linolenic acid losses on *trans* isomerization.

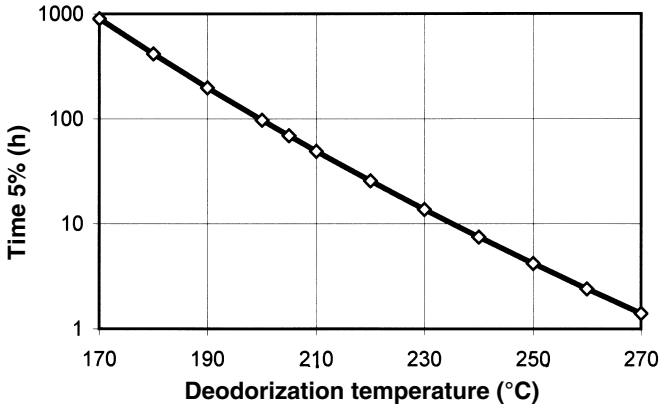

FIG. 8. Time needed to form 5% of *trans* 18:3.

To obtain the highest ratio *R*, an initial oil with a high linolenic acid content and a low linoleic acid content is necessary. The fact that the initial fatty acid composition of the oil has basic effect on the value of *R* explains why canola oil was better than soybean oil for this selective isomerization.

The model defined in this study to describe the isomerization occurring during deodorization has been successfully applied in the Cereol Research Centre in Budapest (Hungary) for the pilot-scale production of the selectively isomerized oil required for the European project. Those results will be the subject of Part II of this paper.

This model can be a useful tool for the optimization of industrial deodorization used in edible oil refining to keep the *trans* isomer content at a low level, which is more and more important as a contemporary quality criterion.

Very mild conditions should be applied to produce a refined oil without significant amounts of geometrical isomers, which could be inconsistent with the goal of refining, e.g., production of a bland and stable oil. The theoretical curves drawn in Figures 9 and 10 for linoleic and linolenic acids could help refiners to predict and control the degree of isomerization during industrial processing.

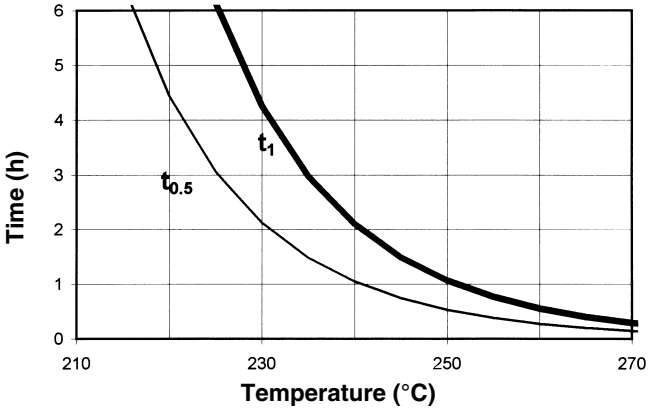

FIG. 9. Linoleic acid: time required to reach degrees of isomerization of 0.5% ($t_{0.5}$) or 1% (t_1).

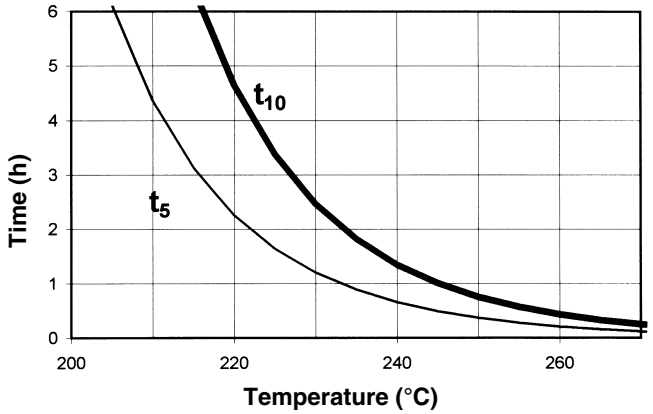

FIG. 10. Linolenic acid: time required to reach degrees of isomerization of 5% (t_5) or 10% (t_{10}).

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[Received May 5, 1998; accepted September 4, 1998]