

# Further Studies on Artificial Geometrical Isomers of $\alpha$ -Linolenic Acid in Edible Linolenic Acid-Containing Oils

Robert L. Wolff\*

Institut des Sciences et Techniques des Aliments de Bordeaux, Université Bordeaux, 33405 Talence Cedex, France

Fifteen samples of commercial edible soybean and rapeseed oils (and mixtures of these) from Belgium, Great Britain and Germany have been analyzed for their *trans*-polyunsaturated fatty acid content. Only one sample out of the 13 refined samples, and the two cold-pressed samples, contained trace amounts of *trans* isomers. Others contained between 1 and 3.3% of their total fatty acids as geometrical isomers of linoleic and linolenic acids. The degree of isomerization (DI) of linolenic acid varied between 10.5 and 26.9%. Combining results obtained in this study together with corresponding data for French oils (totalling 21 samples) indicates that the relative percentages of individual linolenic acid geometrical isomers depend on linolenic acid DI. Relationships linking these parameters could be approximated by straight lines, at least for DI's lying between 9 and 30%. Extrapolation to DI = 0 suggests that the relative probabilities of isomerization of double bonds in positions 9, 12, and 15 are 41.7, 6.1 and 52.1%, respectively, at the very beginning of the isomerization reaction. At that time, the probability of a simultaneous isomerization of double bonds in positions 9 and 15 is close to zero. The *t,c,t* isomer is apparently formed *via* the *c,c,t* and the *t,c,c* isomers, the former being somewhat more prone to a second geometrical isomerization than the latter. The relative proportion of the *c,t,c* isomer is practically independent from the DI, at least between 9 and 30%, which would suggest that this isomer is an "end-product" of the *cis-trans* isomerization reaction.

**KEY WORDS:** Fatty acid composition, geometrical isomerization, linoleic acid, linolenic acid, oil deodorization, rapeseed oil, soybean oil, *trans* isomers.

In a general survey of refined edible linolenic acid-containing oils (rapeseed, soybean and walnut oils) marketed in France (1,2), we have observed that practically all samples contain geometrical isomers of linoleic (*cis-9,cis-12* 18:2) and linolenic (*cis-9,cis-12,cis-15* 18:3) acids (1,2). These unnatural isomers may account for as much as 3.5% of total fatty acids in the oils (1), which is about 31 g/L. Linolenic acid geometrical isomers (LAGIs) were also detected in foods containing these oils (1,3). These isomers are formed during the deodorization of oils (4,5), an operation generally conducted at 230–250°C (or even higher) for several hours, in the presence of steam and under vacuum. Consequently, deodorized rapeseed and soybean oils, which represent between one-quarter and one-third of the oils annually consumed in France (6), are the main dietary sources of LAGIs.

To compare the alteration status of French oils with that of oils from other European countries, we have extended our study to rapeseed and soybean oils marketed in Belgium, Great Britain and Germany. Data presented in our previous reports (1,2) seemed to indicate that LAGIs display an almost invariable pattern with constant individual relative

proportions. However, a more detailed analysis of these data together with the data presented here shows that these proportions are somewhat dependent on the degree of isomerization (DI) of linolenic acid (ratio of the percentage of total LAGIs to the percentage of total octadecatrienoic acids, times 100). Consequently, we tried to establish the relations between the relative percentages of individual LAGIs and linolenic acid DI's.

## EXPERIMENTAL PROCEDURES

**Samples and chemicals.** Rapeseed and soybean oils were purchased from supermarkets and retail food outlets in York (Great Britain), Ath (Belgium), Kehl and Sarrebrücken (Germany) (Table 1). Linolenic and linoleic acid geometrical isomers were prepared by chemical isomerization of linseed oil (7).

**Preparation of fatty acid methyl esters (FAME).** A 12% (wt/vol) solution of BF<sub>3</sub> in methanol (1.5 mL) (Fluka, Buchs, Switzerland) is added to 2 drops of oil, and the resulting mixture is homogenized with benzene (8). The reaction is performed at 100°C for 1 h. After adding water (1.5 mL), FAME are extracted twice with 2.5 mL portions of hexane (8).

**Gas-liquid chromatography (GLC).** Analyses of FAME by GLC were carried out on a Carlo Erba 4130 chromatograph fitted with a flame-ionization detector and a split injector (Carlo Erba, Milano, Italy). A fused silica capillary column coated with 100% cyanopropyl polysiloxane (CP Sil 88, 50 m × 0.33 mm i.d., 0.24 μm film; Chrompack, Mid- delburg, Holland) was used with helium as carrier gas at an inlet pressure of either 0.8 or 1.0 kg/cm<sup>2</sup>. In the first case, the column was operated isothermally at 150°C for 50 min. The temperature was then increased at a rate of 7.5°C/min up to 195°C and held at this temperature until completion of the analysis (7). In the second case, the column was operated isothermally at 175°C for 16 min. The temperature was then increased at a rate of 7.5°C/min up to 195°C and held at this temperature until completion of the analysis (2). In both cases, the injection port and the detector were maintained at 250°C. Identification of individual isomers in the oils was realized with elaidinized linseed oil FAME as reference compounds (7). Quantitative analyses were performed with an SP 4290 integrator (Spectra Physics, San Jose, CA).

## RESULTS AND DISCUSSION

A partial chromatogram of FAME prepared with rapeseed oil (sample GB4) is given in Figure 1. Identification of peaks was made as described elsewhere (7). This tracing was obtained with the CP Sil 88 capillary column operated at 150°C with a carrier gas pressure of 0.8 kg/cm<sup>2</sup>. In such conditions, the *t,c* isomer of linoleic acid may not be fully separated from the main all-*cis* peak, mainly when soybean oils are analyzed. A better resolution between these two isomers is achieved by increasing both the temperature and the carrier gas pressure (see the Experimental Procedures section). However, under these con-

\*Address correspondence at ISTAB, Laboratoire de Lipochimie Alimentaire, Université Bordeaux I, Allée des Facultés, 33405 Talence Cedex, France.

TABLE 1

## Identification and Commercial Origin of Oil Samples

Sample code <sup>a</sup>	Oil <sup>b</sup>	Trademark	Sample code	Oil	Trademark
B1	SBO	Vandemoortele	GB2	SBO	Safeway
B2	SBO	Delhaize	GB3	RSO	Goldenfields
B3	SO	Delhaize	GB4	SBO	Sainsbury's
B4	SBO	Match	GB5	VO	Morrisons
B5	SBO	Meteor	G1	RSO*	Vitaquell
B6	SBO	Nopri	G2	SBO*	Vitaquell
B7	SBO	Imperiale	G3	VO	Brölio
GB1	RSO	Sainsbury's			

<sup>a</sup>B, Belgian oils; GB, British oils; G, German oils.

<sup>b</sup>Nature of the oils as mentioned on the labels. SBO, soybean oil; RSO, rapeseed oil; SO, salad oil; VO, vegetable oil. Abbreviations followed by an asterisk correspond to cold-pressed oils.

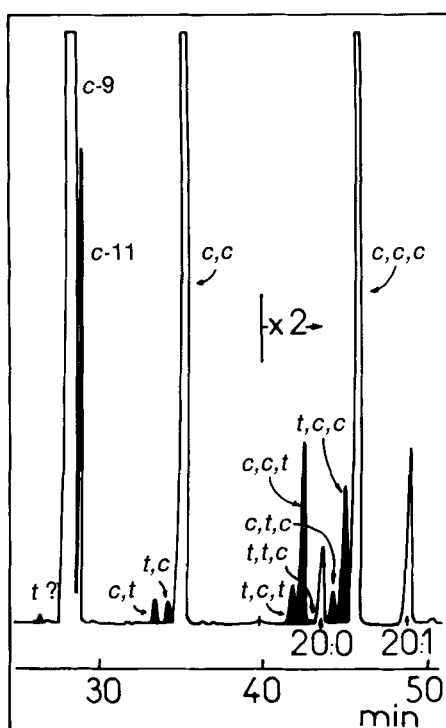


FIG. 1. Partial chromatogram of fatty acid methyl esters prepared with a sample of British rapeseed oil (sample GB4). Analysis on a CP Sil 88 capillary column operated at 150°C with a carrier gas pressure of 0.8 kg/cm<sup>2</sup> (c, *cis*; t, *trans*).

ditions, the *c,t,c* isomer is no longer separated from the *t,c,c* peak, and the 20:1 acid is partly fused with the trailing edge of the main all-*cis* isomer of linoleic acid (results not shown). It was thus necessary to combine data obtained under both kinds of conditions to quantitate all individual *trans* isomers.

The fatty acid compositions of rapeseed and soybean oils (and of mixtures of these oils) from Belgium (7 samples), Great Britain (5 samples) and Germany (3 samples) are presented in Table 2. Except for the two German cold-pressed oils, only one sample (B7) out of the 13 other samples under study does not show appreciable levels of LAGIs. This proportion is almost the same as that ob-

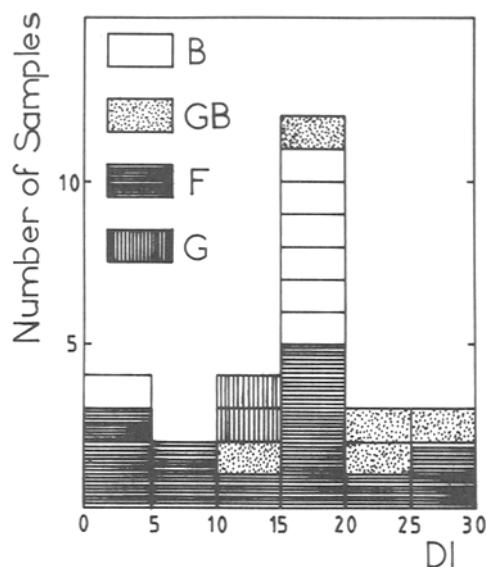


FIG. 2. Distribution of oil samples (rapeseed oils, soybean oils, mixtures of these, walnut oils) as a function of their linolenic acid degree of isomerization (DI) (B, Belgium; GB, Great Britain; F, France; G, Germany).

served for French oils (1) and foods containing such oils (1,3). For the four European countries (12, 7, 5 and 1 samples, respectively, French, Belgian, British and German rapeseed and soybean oils), and if one includes data for refined walnut oils [3 samples (2)], thus totalling 28 samples, the proportion of altered commercial fully refined oils (containing more than trace amounts of *trans*-polyunsaturated fatty acids) is about 90%. The diagram in Figure 2 shows that about 40% of the European samples present a DI of between 15 and 20% and 65% of these samples have a DI higher than 15%. About 20% of the samples have a DI lower than 10%.

Although commercialized under different trademarks, samples B4 and B5 (Table 2) display similar fatty acid compositions. Since the suppliers' addresses on the labels were the same, it was concluded that these two samples come from the same soybean oil batch. Comparison of their fatty acid compositions gives a good idea of the accuracy of our analytical method (GLC of FAME under two kinds of conditions) and fully justifies the use of two figures after the decimal point in our calculations.

Values of linolenic acid DI's are rather homogeneous for Belgian oils: 15.8 to 19.4 (Table 3). On the contrary, corresponding values for British oils are more variable: from 14.6 to 26.9. French oils showed an even more heterogeneous distribution of DI's: from 2.3 to 29.6 (1). However, the relative percentages of individual LAGIs are not very different from one sample to another (Table 3). Ranges for the *c,c,t*, *c,t,c* and *t,c,c* isomers in Belgian oils are 47.2–48.9, 6.4–7.5 and 40.7–42.2%, respectively. Corresponding values for British oils are 44.2–50.1, 6.7–7.8 and 38.0–41.0%, and for French oils, 45.8–51.6, 5.4–7.5 and 39.0–42.0% (1). Similar ranges were also noted in refined walnut oils from France and Germany: 49.2–52.9, 6.2–7.8 and 38.1–41.9% (2). Taking into account all available data (24 samples: 10 samples from reference 1,

## 18:3n-3 ACID ISOMERS IN OILS

TABLE 2

Fatty Acid Composition of Commercial Rapeseed and Soybean Oils from Belgium, Great Britain and Germany

Fatty acid	Samples						
	B1 <sup>a</sup>	B2	B3	B4	B5	B6	B7
	(SBO) <sup>b</sup> (n = 4) <sup>c</sup>	(SBO) (n = 4)	(RSO + SBO) (n = 4)	(SBO) (n = 4)	(SBO) (n = 4)	(SBO) (n = 4)	(SBO) (n = 2)
14:0	0.08 <sup>d</sup>	0.07	0.05	0.08	0.08	0.08	0.08
16:0	10.65	10.46	4.87	10.51	10.72	10.46	10.45
16:1	0.09	0.09	0.26	0.08	0.09	0.09	0.08
17:0	0.08	0.10	0.05	0.09	0.08	0.08	0.08
18:0	3.71	3.82	1.52	3.81	3.77	3.59	3.75
<i>t</i> <sup>e</sup> 18:1	trace <sup>f</sup>	trace	0.06	0.06	trace	trace	trace
<i>c</i> -9 18:1	21.15	18.94	54.84	22.48	22.35	21.79	21.14
<i>c</i> -11 18:1	1.37	1.27	3.42	1.40	1.45	1.50	1.38
<i>c</i> -9, <i>t</i> -12 18:2	0.36	0.41	0.18	0.38	0.38	0.41	0.05
<i>t</i> -9, <i>c</i> -12 18:2	0.29	0.34	0.13	0.32	0.31	0.29	trace
<i>c</i> -9, <i>c</i> -12 18:2	54.09	55.05	21.21	53.01	53.02	53.43	54.65
<i>t</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	0.04	0.06	0.06	0.04	0.04	0.05	trace
<i>c</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	0.52	0.76	0.90	0.53	0.52	0.59	0.04
<i>c</i> -9, <i>t</i> -12, <i>c</i> -15 18:3	0.08	0.12	0.13	0.07	0.07	0.09	—
<i>t</i> -9, <i>c</i> -12, <i>c</i> -15 18:3	0.44	0.67	0.75	0.46	0.46	0.51	0.04
<i>c</i> -9, <i>c</i> -12, <i>c</i> -15 18:3	5.74	6.71	7.86	5.26	5.26	5.69	7.13
20:0	0.39	0.33	0.60	0.39	0.38	0.39	0.35
<i>c</i> -11 20:1	0.21	0.17	1.48	0.21	0.21	0.24	0.21
22:0	0.48	0.38	0.40	0.50	0.48	0.47	0.46
<i>c</i> -13 22:1	trace	trace	0.91	trace	trace	trace	trace
Others <sup>g</sup>	0.23	0.25	0.32	0.32	0.33	0.25	0.11

Fatty acid	GB1	GB2	GB3	GB4	GB5	G1	G2	G3
	(SBO)	(SBO)	(RSO)	(RSO)	(RSO + SBO)	(RSO*)	(SBO*)	(RSO)
	(n = 3)	(n = 4)	(n = 5)	(n = 4)	(n = 4)	(n = 2)	(n = 2)	(n = 2)
14:0	0.07	0.08	0.04	0.04	0.05	0.06	trace	0.05
16:0	10.15	10.68	4.81	4.97	6.02	5.24	10.12	4.67
16:1	0.09	0.09	0.25	0.27	0.20	0.16	0.08	0.26
17:0	0.09	0.09	0.05	0.05	0.05	0.05	0.08	0.04
18:0	3.63	3.59	1.49	1.52	1.94	2.27	3.90	1.64
<i>t</i> 18:1	trace	0.05	0.06	0.07	0.05	0.05	0.04	0.09
<i>c</i> -9 18:1	23.89	22.40	54.48	53.67	49.68	46.68	21.81	59.04
<i>c</i> -11 18:1	1.51	1.51	3.32	3.55	2.78	2.24	1.21	3.30
<i>c</i> -9, <i>t</i> -12 18:2	0.51	0.47	0.14	0.32	0.19	0.10	0.04	0.07
<i>t</i> -9, <i>c</i> -12 18:2	0.38	0.40	0.10	0.27	0.16	0.05	—	0.05
<i>c</i> -9, <i>c</i> -12 18:2	51.10	51.82	21.79	21.73	26.78	32.65	53.95	19.24
<i>t</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	0.08	0.11	0.05	0.27	0.05	trace	—	0.03
<i>c</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	0.71	0.77	0.77	1.21	0.75	0.06	trace	0.46
<i>c</i> -9, <i>t</i> -12, <i>c</i> -15 18:3	0.11	0.11	0.10	0.22	0.12	—	—	0.05
<i>t</i> -9, <i>c</i> -12, <i>c</i> -15 18:3	0.62	0.66	0.62	1.04	0.64	0.04	trace	0.37
<i>c</i> -9, <i>c</i> -12, <i>c</i> -15 18:3	5.64	5.63	9.03	7.45	7.83	8.25	7.46	7.79
20:0	0.36	0.35	0.56	0.57	0.57	0.47	0.33	0.62
<i>c</i> -11 20:1	0.29	0.27	1.32	1.39	1.17	0.92	0.28	0.31
22:0	0.44	0.42	0.40	0.40	0.46	0.38	0.36	0.37
<i>c</i> -13 22:1	0.04	trace	0.11	0.44	0.22	0.10	trace	0.31
Others	0.29	0.50	0.41	0.55	0.29	0.23	0.34	0.09

<sup>a</sup>Bx, GBx and Gx, oil samples from Belgium, Great Britain and Germany, respectively.<sup>b</sup>SBO and RSO, samples of soybean and rapeseed oils, respectively. Samples with an asterisk are cold-pressed oils.<sup>c</sup>Number of analyses.<sup>d</sup>Results are expressed as peak area percentages.<sup>e</sup>*t*, trans: *c*, cis.<sup>f</sup>Trace amounts (peaks visible on chromatograms, but not taken into account by the integrator).<sup>g</sup>Sum of minor identified or unknown components.

3 from reference 2 and 11 from this study), mean values for the *c,c,t*, *c,t,c* and *t,c,c* isomers are  $48.0 \pm 1.7$ ,  $6.8 \pm 0.7$  and  $40.8 \pm 1.2\%$ . These values are identical to our initial estimations (1). Apparently, these percentages can thus be considered as constant.

However, two observations led us to modify our first conclusion concerning this apparent constancy. First, the

surprisingly high level of the *t,c,t* isomer in sample GB4 (10.0%) is quite different from the mean value calculated for French (1), Belgian or other British rapeseed and soybean oils ( $4.9 \pm 1.5\%$ ,  $3.7 \pm 0.2\%$  and  $3.8 \pm 0.3\%$  of total LAGIs, respectively). Second, we have observed that heating a cold-pressed walnut oil under vacuum at 230°C for 3 h generates only trace amounts of the *t,c,t* isomer

TABLE 3

Relative Percentages and Degrees of Isomerization of Linoleic and Linolenic Acid Geometrical Isomers (containing at least one *trans* double bond) in Commercial Rapeseed and Soybean Oils from Belgium, Great Britain and Germany

	Samples <sup>a</sup>					
	B1 (SBO)	B2 (SBO)	B3 (RSO + SBO)	B4 (SBO)	B5 (SBO)	B6 (SBO)
Total <i>trans</i> 18:2 <sup>b</sup>	0.65	0.75	0.31	0.70	0.69	0.70
Total 18:2	54.74	55.70	21.52	53.71	53.71	54.13
DI 18:2 <sup>c</sup>	1.19	1.35	1.44	1.30	1.28	1.29
<i>c</i> -9, <i>t</i> -12 18:2 <sup>d</sup>	55.4	54.7	58.1	54.3	55.1	58.6
<i>t</i> -9, <i>c</i> -12 18:2	44.6	45.3	41.9	45.7	44.9	41.4
Total <i>trans</i> 18:3	1.08	1.61	1.84	1.10	1.09	1.24
Total 18:3	6.82	8.32	9.70	6.36	6.35	6.93
DI 18:3	15.84	19.35	18.97	17.30	17.17	17.89
<i>t</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	3.7	3.7	3.3	3.6	3.7	4.0
<i>c</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	48.2	47.2	48.9	48.2	47.7	47.6
<i>c</i> -9, <i>t</i> -12, <i>c</i> -15 18:3	7.4	7.5	7.1	6.4	6.4	7.3
<i>t</i> -9, <i>c</i> -12, <i>c</i> -15 18:3	40.7	41.6	40.8	41.8	42.2	41.1
DI 18:3/DI 18:2	13.31	14.33	13.17	13.31	13.41	13.87
	GB1 (SBO)	GB2 (SBO)	GB3 (RSO)	GB4 (RSO)	GB5 (RSO + SBO)	G1 (RSO)
Total <i>trans</i> 18:2	0.91	0.87	0.24	0.59	0.35	0.12
Total 18:2	51.99	52.69	22.03	22.32	27.13	19.36
DI 18:2	1.71	1.65	1.09	2.64	1.29	0.65
<i>c</i> -9, <i>t</i> -12 18:2	57.3	54.0	58.3	53.4	54.3	58.3
<i>t</i> -9, <i>c</i> -12 18:2	42.7	46.0	41.7	46.6	45.7	41.7
Total <i>trans</i> 18:3	1.52	1.65	1.54	2.74	1.56	0.91
Total 18:3	7.16	7.28	10.57	10.19	9.39	8.70
DI 18:3	21.29	22.66	14.57	26.89	16.61	10.46
<i>t</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	5.3	6.7	3.0	10.0	3.2	3.3
<i>c</i> -9, <i>c</i> -12, <i>t</i> -15 18:3	46.7	46.7	50.1	44.2	48.1	50.5
<i>c</i> -9, <i>t</i> -12, <i>c</i> -15 18:3	7.2	6.7	6.7	7.8	7.7	5.5
<i>t</i> -9, <i>c</i> -12, <i>c</i> -15 18:3	40.8	40.0	40.2	38.0	41.0	40.7
DI 18:3/DI 18:2	12.45	13.73	13.37	10.19	12.88	16.09

<sup>a</sup>Abbreviations for samples and fatty acids as in Table 1.

<sup>b</sup>Percentages of total *trans* 18:2, total 18:2, total *trans* 18:3 and total 18:3 acids are relative to the sum of all fatty acids.

<sup>c</sup>DI, degree of isomerization for the indicated fatty acid ratio of total *trans* 18:2 (or *trans* 18:3) on total 18:2 (or 18:3) times 100.

<sup>d</sup>Percentages of individual isomers of a given fatty acid are relative to their total.

TABLE 4

Characteristics of the Equations Describing the Linear Relationships Between the Relative Percentages of Individual Linolenic Acid Geometrical Isomers and the DI of Linolenic Acid

Isomer structure	Slope	Intercept	Correlation factor
<i>c</i> -9, <i>c</i> -12, <i>t</i> -15 <sup>a</sup>	-0.262 <sup>b</sup>	52.67 <sup>c</sup>	-0.90
<i>c</i> -9, <i>t</i> -12, <i>c</i> -15	0.028	6.24	0.20
<i>t</i> -9, <i>c</i> -12, <i>c</i> -15	0.068	42.23	0.36
<i>t</i> -9, <i>c</i> -12, <i>t</i> -15	0.309	-1.27	0.86

<sup>a</sup>*c*, *cis*; *t*, *trans*.

<sup>b</sup>Percentage of a given isomer (relative to total linolenic acid geometrical isomers) per degree of isomerization (DI) unit.

<sup>c</sup>Figures for intercepts correspond to percentages of a given isomer relative to total linolenic acid geometrical isomers.

(less than 2% of total LAGIs) (2). Thus, it becomes evident that the relative percentage of the *t,c,t* isomer can vary with the physical conditions of industrial deodorization. If this isomer can vary from less than 2% up to 10%

of total LAGIs, one or several other isomers must also vary. This is clearly evidenced by plots of relative percentages of individual LAGIs as a function of DI (Fig. 3). These plots are based on data obtained with French oils (oil samples displaying DIs higher than 9%) (1,2) and on data reported in this study, totalling 21 samples. These functions can be approximated by straight lines, with characteristics as indicated in Table 4.

The relative percentage of the *c,t,c* isomer is not correlated, apparently, with the DI (correlation factor: 0.20). Its value remains fairly constant at *ca.* 6.5% for DIs between 9 and 30%. On the other hand, good correlation factors are obtained for the *c,c,t* and *t,c,t* isomers. The first component decreases with increasing DIs, while the second increases (Fig. 3). The *t,c,c* isomer also tends to diminish with increasing DIs. However, the correlation factor is low (Table 4). These tendencies can be interpreted as follows. At the beginning of the isomerization reaction, that is, for DIs close to zero, the probabilities of formation of individual LAGIs are 52.1, 41.7, 6.2 and 0 for the *c,c,t*, *t,c,c*, *c,t,c* and *t,c,t* isomers, respectively. As the reac-

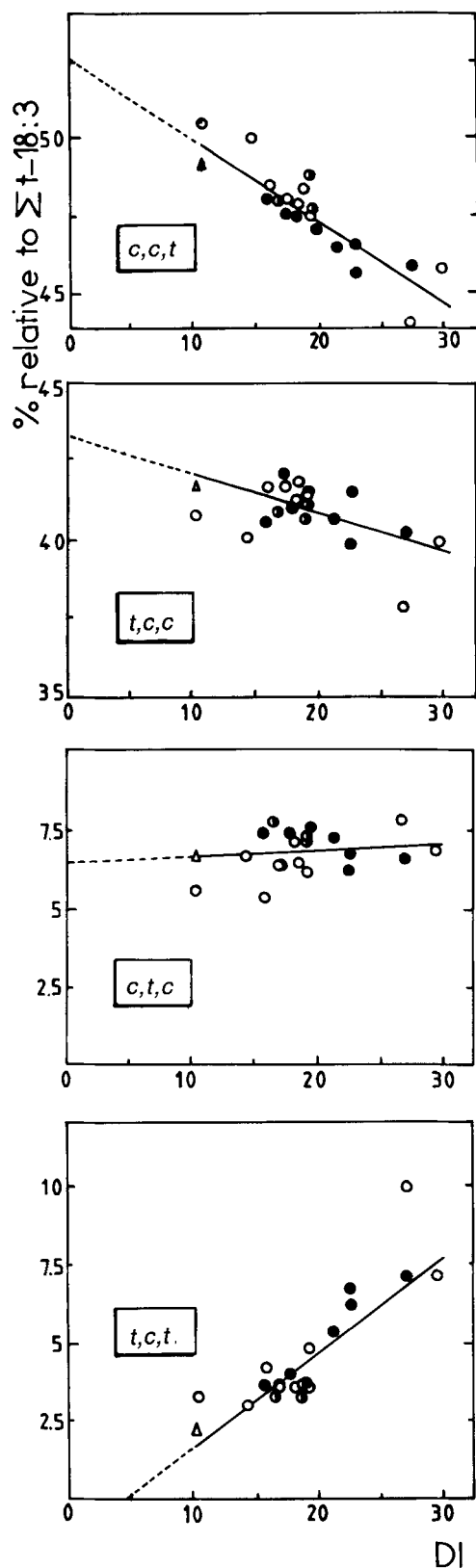


FIG. 3. Plots of the percentages of individual linolenic acid geometrical isomers relative to their sum as a function of linolenic acid degree of isomerization (DI). From top to bottom: *cis*-9,*cis*-12,*trans*-15 18:3, *trans*-9,*cis*-12,*cis*-15 18:3, *cis*-9,*trans*-12,*cis*-15 18:3, and *trans*-9,*cis*-12,*trans*-15 18:3 acids. ○, rapeseed oils; ●, soybean oils; ○, mixtures of rapeseed and soybean oils; △, walnut oil.

TABLE 5

Relative Probability of *cis-trans* Isomerization of Linolenic Acid as Compared to Linoleic acid (DI 18:3/DI 18:2)

Country	Oil	DI 18:3/ DI 18:2	n <sup>a</sup>	Reference
France	RSO, SBO <sup>b</sup>	13.4 ± 1.4	11	1
Belgium	RSO, SBO	13.6 ± 0.4	6	This study
Great Britain	RSO, SBO	12.5 ± 1.4	5	This study
Germany	RSO	16.1	1	This study
France, Germany	WNO	13.5 ± 1.1	3	2
All countries <sup>c</sup>	SBO	13.6 ± 1.3	11	2, This study
All countries	RSO	13.1 ± 1.6	9	2, This study
All countries	All samples <sup>d</sup>	13.4 ± 1.3	26	1, 2, This study

<sup>a</sup>Number of samples.

<sup>b</sup>Abbreviations: RSO, rapeseed oil; SBO, soybean oil; WNO, walnut oil, DI, degree of isomerization.

<sup>c</sup>Include France, Belgium and Great Britain for SBO, and France, Great Britain and Germany for RSO.

<sup>d</sup>Include mixtures of RSO and SBO sold as "vegetable" or "salad" oils.

tion goes forth (when the DI increases), some of the *c,c,t* and *t,c,c* isomers undergo a second isomerization and give rise to the *t,c,t* isomer. This would mean that the formation of the di-*trans* isomer follows two-step kinetics. According to data in Table 4, the *t,c,t* would be formed preferentially *via* the *c,c,t* isomer (*ca.* 85%). On the other hand, the proportion of the *c,t,c* isomer does not evolve with the DI. This isomer may thus be an end product of the *cis-trans* isomerization reaction.

The probability of isomerization of linolenic acid as compared to that of linoleic acid equals  $13.4 \pm 1.3$ . As can be seen in Table 5, this value is independent of either the nature of the oil or its country of origin. This means, at least for DIs between 9 and 30%, that this ratio is rather insensitive to either the initial linolenic acid content of the oil (and more generally to its fatty acid composition) or the physical conditions of deodorization (geometrical characteristics of the apparatuses, temperatures and times of heating). The relative proportions of the mono-*trans* isomers of linoleic acid are practically constant (Table 3). If one considers the ratio of the *cis*-9,*trans*-12 isomer relative to total *trans* isomers of linoleic acid, values of  $54.7 \pm 3.3\%$ ,  $55.9 \pm 1.7\%$ ,  $55.5 \pm 2.2\%$  and  $58.3\%$  can be calculated for French (1), Belgian, British and German oils, respectively. For all samples, including walnut oils (2) and totalling 25 samples, a general mean of  $55.9 \pm 2.9\%$  can be calculated. The ethylenic bond nearest the carboxylic group seems thus to be slightly less reactive than the ethylenic bond nearest the carboxylic group on the methyl side of the molecule. This is also true for the *c,c,t* and *t,c,c* isomers of linolenic acid. If one considers the *c,c,t*/(*c,c,t* + *t,c,c*) ratio at the beginning of the isomerization reaction, a value of 54.7% can be calculated. However, if all values are taken into account, a slightly different mean is obtained:  $53.8 \pm 0.7$ . There too, and relative to the carboxylic group, the proximal double bond appears to be less reactive than the distal one.

One should be aware of the fact that all relationships established in this study may not be of predictive value. For example, if oils that have been deodorized under different conditions are mingled in the same tank, the

resulting *trans* isomer content may not fit the equations given in this study. Such mixtures may also be responsible for the dispersion of analytical results displayed in this study. They may also explain the presence of trace amounts of *trans* isomers in cold-pressed oils, if such oils have been stored in unswept tanks. Also, heating in the deodorizers may be heterogeneous. This will lead to a mixture of differently heated oils. To get rid of such parameters, we are currently studying the geometrical isomerization of linolenic acid in a model oil, that is, flaxseed oil, under controlled conditions.

#### ACKNOWLEDGMENTS

The author thanks Florence Caralp, Frederic F. Vandamme, Guy B. Wolff and Pierre Wolff for purchasing and sending the oil samples.

#### REFERENCES

1. Wolff, R.L., *J. Am. Oil Chem. Soc.* 69:106 (1992).
2. Wolff, R.L., *Sci. Alim.* 13:155 (1993).
3. Wolff, R.L., and J.-L. Sebedio, *J. Am. Oil Chem. Soc.* 68:719 (1991).
4. Ackman, R.G., S.N. Hooper and D.L. Hooper, *Ibid.* 51:42 (1974).
5. Devinat, G., L. Scamaroni and M. Naudet, *Rev. Fr. Corps Gras.* 27:283 (1980).
6. Anonymous, *INFORM* 12:1078 (1991).
7. Wolff, R.L., *J. Chromatogr. Sci.* 30:17 (1992).
8. Morrison, W.R., and L.M. Smith, *Lipids* 5:600 (1965).

[Received August 27, 1992; accepted January 1, 1993]