Degradation of α-Linolenic Acid During Heating

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ABSTRACT: Degummed bleached rapeseed oil was heated at 210, 220, and 230°C for up to 86 h under reduced pressure with nitrogen stripping. No significant change of total linoleic acid content was found, but a decrease of the total linolenic acid content was observed under extreme conditions. The degradation rate of linolenic acid is described as a function of heating time and operating temperature. Linolenic acid degradation can be predicted for any set of conditions by the established model. No significant degradation of linolenic acid can occur under standard deodorization conditions.

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KEY WORDS: Degradation, deodorization, heating, kinetics, linoleic acid, linolenic acid, modeling.

Vegetable oils are refined by means of alkali- or physical refining. In both industrial processes, the last step consists of heating the oil for 1 to 4 h at a high temperature (180–260°C), under low pressure (1–10 mbar), with steam or nitrogen injection. The effects of processing on minor components of oils, such as sterols, steryl esters, tocopherols, polymeric triglycerides and *trans* fatty acids, have been thoroughly investigated (1), but little information is available on degradation of polyunsaturated fatty acids during deodorization.

Studies about refined oils that are subjected to long-term heat treatment mainly cover the user's point of view, e.g., heating in the presence of air and deep-frying of different foods. These papers focus on the measurement of free fatty acids, conjugated dimers and trimers, polymeric triglycerides, and *trans* fatty acid isomers (2–5). Also data related to fatty acid degradation can be found (6–9).

In previous laboratory experiments at Lesieur Research and Development Center (Coudekerque-Branche, France), in addition to the isomerization of the polyunsaturated fatty acids, a decrease in the linolenic acid content was observed during long-term heating under vacuum, depending on time and temperature.

To complete the study, special heating trials with extremely long residence time were carried out on a pilot scale for investigation of the degradation kinetics.

EXPERIMENTAL PROCEDURES

Experiments. The experiments were carried out in the pilot plant refinery of Cereol Group Research and Development Centre in Budapest (Hungary). Degummed and bleached oil was supplied by the Cereol physical refinery of Martfu (Hungary); the fatty acid composition of this treated oil was as follows: 16:0, 4.8%; 16:1, 0.2%; 18:0, 1.8%; 18:1, 60.1%; 18:2, 21.3%; 18:3, 8.3%; 20:0, 0.6%; 20:1, 1.3%; 22:0, 0.4%; 22:1, 0.4%; and unidentified, 0.8%. Heating of the oil was performed at 1.5 mbar pressure at 210, 220, and 230°C for 86, 48, and 24 h, respectively, in a pilot-scale batch deodorizer. In all three experiments, 100 L of oil were heated, under reduced pressure (<2 mbars) and nitrogen stripping, up to the operating temperature (±1°C). Continuous heating lasted from 24 to 86 h, depending on the temperature. Samples were taken for the analysis of the fatty acid composition every 2 h through a cooled sampling system.

Determination of total fatty acid composition. Fatty acid methyl esters (FAME) were prepared according to the official method AOCS Ce 2-66 (10) and analyzed on a 5890 Series II plus gas chromatograph (Hewlett-Packard; Palo Alto, CA), equipped with an electronic pressure control system, a split/splitless injector (210°C), and a flame-ionization detector set at 210°C. Separations were performed on a SP2340 fused-silica capillary column (60 m × 0.25 mm i.d., 0.2 µm film; Supelco, Inc., Bellefonte, PA). Hydrogen

TABLE 1
Total Linoleic and Linolenic Acid Content as a Function of Heating Time and Temperature

Heating time (h)[a]	Total linoleic acid, $C_{18:2}$ (%)[b]			Total linolenic acid, $C_{18:3}$ (%)[b]		
	210°C[c]	220°C[c]	230°C[c]	210°C[c]	220°C[c]	230°C[c]
0	21.2	21.4	20.9	8.3	8.4	8.3
8	21.0	21.8	21.0	8.3	8.1	8.0
16	21.0	21.0	20.9	8.2	8.2	8.0
24	20.9	21.1	20.8	8.1	8.0	7.7
32	20.9	20.6		8.1	7.8	
40	21.3	20.8		8.0	7.8	
48	21.2	20.7		7.9	7.8	
62	21.0			7.9		
86	20.9			7.8		

[a]Heating time is zero when the operating temperature is reached.
[b]Fatty acid methyl esters expressed in percentage of total peak area.
[c]Heating temperature.

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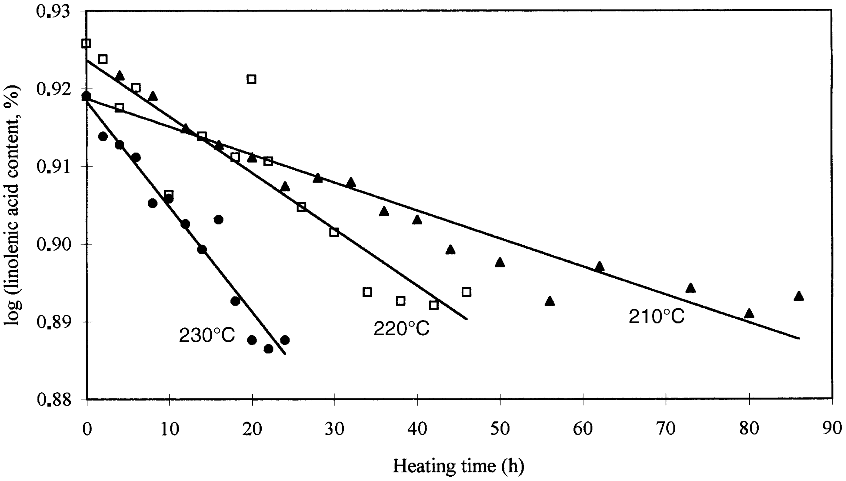

FIG. 1. Effect of temperature on linolenic acid degradation.

was used as the carrier gas at a constant rate of 19.8 cm/s. Gas chromatographic operating conditions were: initial oven temperature 150°C for 0.1 min, temperature programmed to 200°C at 1.3°C/min, final temperature 200°C for 10 min. The gas chromatograph was calibrated with an external standard, consisting of a mixture of 79% heptadecanoic acid methyl ester and 21.0% eicosanoic acid methyl ester (each methyl ester obtained from Sigma-Aldrich, Budapest, Hungary). Quantitative analysis was performed with a Hewlett-Packard Chemstation 3365 software.

Statistics. Linear regressions were calculated with Microsoft Excel 5.0 (Redmond, WA).

RESULTS AND DISCUSSION

Table 1 summarizes part of the experimental results obtained. The small variations of the linoleic acid content are not significant. Thus, we can assume that no degradation of that fatty acid occurs during the process, even at higher temperatures up to 270°C, as was shown in previous laboratory trials. On the contrary, the evolution of the linolenic acid content at each temperature (Fig. 1) shows a linear relationship between the logarithm of the linolenic acid content at time t (C_t) and the heating duration (t). The linolenic acid degradation is well described by the following equation:

$$\log C_t = -k_d t + \log C_0 \qquad [1]$$

where k_d is the degradation coefficient (h^{-1}), and C_0 is the initial linolenic acid content of the oil. This linear relation indicates that linolenic acid degradation during heating is a first-order reaction.

The degradation coefficient measured as the slope of the regression straight lines varies from 3.5×10^{-4} to $13.5 \times 10^{-4}\ h^{-1}$ at 210–230°C and is a function of the reciprocal of the absolute temperature (T), according to Equation 2 (Fig. 2):

$$\log k_d = -(k_t/T) + b \qquad [2]$$

where k_t is the temperature coefficient (°K), and b is a constant value. Once k_t and b have been determined for a given equipment (in this experiment, 7121 K and 11.3, respectively, Fig. 2), it is possible to predict the linolenic acid content modifications in every set of conditions used.

The calculated degradation coefficients from the equations obtained for the Cereol pilot deodorizer (given in Table 2) are in good agreement with the values previously measured by Lesieur R&D with a home-made semi-pilot deodorizer, where no difference was observed between steam and nitrogen injection. These calculations are of interest when studying the degradation of polyunsaturated fatty acids under industrial conditions. No significant degradation should be observed under adequate processing parameters (Fig. 3).

The results presented in this paper were obtained within the framework of a European Union project concerning the health and nutritional impact of *trans* polyunsaturated fatty acids. The role of Lesieur and Cereol R&D in this project was the production of special, selectively isomerized rapeseed oil, which required a detailed kinetic study. The results on the kinetics of geometrical isomer formation will be the subject of a separate article.

TABLE 2
Degradation Coefficients of Linolenic Acid in Rapeseed Oil ($\times 10^4 h^{-1}$)

		Calculated[b]	
Temperature (°C)	Measured[a]	Cereol pilot plant	Lesieur laboratory
210	3.5	3.5	3.4
220	6.9	6.9	7.2
230	13.5	13.5	14.9
250			58.3
270			208.6

[a] Equation 1.
[b] Equation 2.

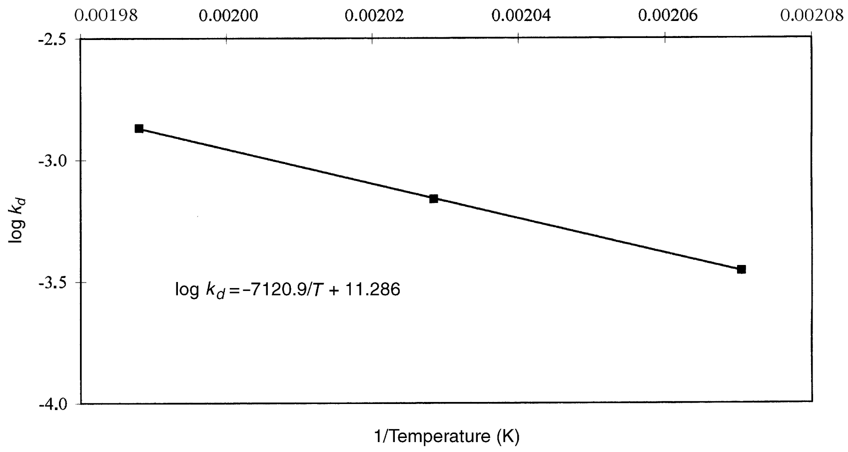

FIG. 2. Effect of temperature on the degradation coefficient k_d.

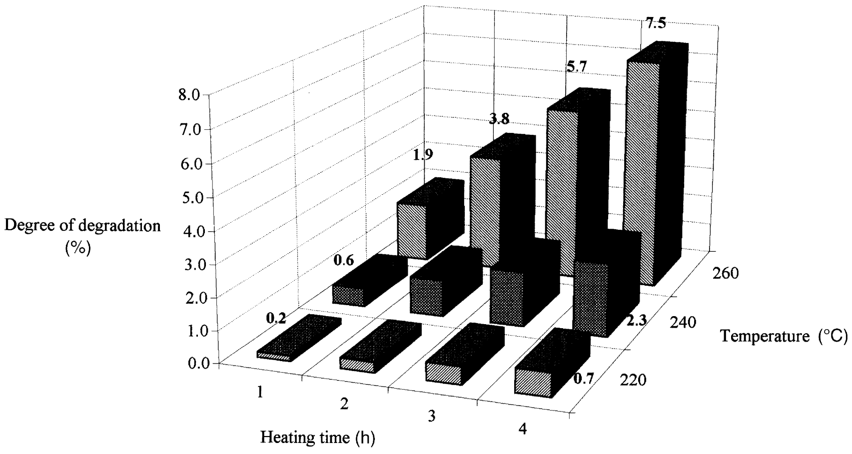

FIG. 3. The degree of degradation is defined as $(1 - C_t/C_0)100$, where C_0 is the initial linolenic acid content and C_t is the linolenic acid content at time t.

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