The Effect of Heat Treatment on Fatty Acids of Rapeseed Oils

B. Leszkiewicz* and **M. Kasperek**
Institute of Commodity Sciences, Academy of Economics in Poznań, Poland

Changes were followed in raw, refined and hydrogenated rapeseed oils subjected to an eight-hr heating under isothermal conditions within 110–200 C. The oils underwent oxidation, polymerization and changes in unsaturation, the extent of the above changes depending essentially on the kind of oil and the temperature applied.

The effect of heating on the biological value of oils and fats may be either beneficial or detrimental depending, to a high degree, on the temperature used. As shown by feeding experiments certain oils subjected to mild heat treatment reduce the amounts of carbonyl compounds in reserve fats of animals (1), promote the growth and longevity of animals (2), and show tumor-inhibiting properties (3). Severe heating (frying, roasting) has been shown to damage the nutritive value of oils and fats, giving rise to the formation of such products as peroxides, oxypolymers, ring monomers, carbonyls and others (4-6). In the studies carried out this far on the practical applicability of individual fats and oils, the kinetic approach to the physicochemical changes at early stages of heat processing has not been given adequate attention.

MATERIALS AND METHODS

The study was carried out on samples of high erucic rapeseed oil taken at different stages of the margarine making-process, raw, refined and hydrogenated oils.

The samples were heated in open glass vessels, 21 cm i.d. and with a layer of oil 5 cm thick. The heating temperatures were 110, 130, 150, 180 and 200 C, and the time of heating eight hr. The analytical samples were taken every 60 min.

Quantitative changes in peroxides were followed according to Lea (7).

The analysis of fatty acids was effected by gas chromatography (GC) using a Varian gas chromatograph with a flame ionization detector (FID). The operating conditions were: column 91.44 cm × 2 mm; Chromosorb W with 10% PEGA; 195 C; carrier gas, nitrogen; detector, 250 C; injector, 225 C.

Changes in dynamic viscosity were established by means of a rotary viscosimeter Rheotest 2. The same instrument and CCl_4 solutions of the oils examined were used to follow changes in mean molecular weight (MMW). MMW was calculated from the viscosity of solution of oil in CCl_4 according to Mark-Houwink:

$$\frac{\eta - \eta_0}{\eta_0 \cdot c} = K \cdot M^{\alpha} \qquad [1]$$

where: η = viscosity of solution; η_0 = viscosity of solvent; c = concentration of oil (g/100 cm^3), and α = the constant characteristic of the system. Its value assumed for the system used amounted to 0.5.

The value of the constant K, as calculated from Equation [1] for the system : stearic acid − CCl_4, amounted to 0.00165.

The rate and extent of *cis-trans* isomerization were examined by infra-red (IR) technique (7).

Nuclear magnetic resonance (NMR) was used to follow quantitative changes in protons within the following carbon atoms: $C\underline{H}C\underline{H}$ 5.27, $C\underline{H}_2O$ 4.13, $CHC\underline{H}_2$ 2.73, $C\underline{H}_2COO$ 2.18, $C\underline{H}_3$ 0.88. The analysis was effected with a Varian EM 360 apparatus, 60 MHz, CCl_4 solutions of the fats tested were used. The number of protons was calculated in relation to methylene protons of glycerol, the number of which was assumed to be four.

RESULTS AND DISCUSSION

Taking into account both the character and extent of changes in the oils, the results should be discussed separately for each of the two temperature ranges, 110–150 C and 150–200 C.

According to the peroxide values obtained with the samples heated within the temperature range 110–150 C, the rate of oxidation depended essentially on the temperature and time heating; higher temperatures and longer heating time gave higher concentrations of peroxides (Fig. 1).

The oils examined varied in their resistance to oxidation. The samples of raw oil were more resistant to oxidation than those of refined oil. A high oxidative stability was stated for the samples of hydrogenated oil heated at 110 C up to the eighth hour and at 130 C up to the seventh hour of heating. This proved the hydrogenated oil to be more resistant to oxidation than the remaining oils studied, provided that the heating time was dept within the induction period. Beyond the induction period a sharp increase in peroxides was observed.

The effect of heating temperatures 110–150 C on the composition of fatty acids varied depending on the kind of oil. As to raw oil a temporary increase in linoleic and linolenic acids occurred in the first stage of heating, this being particularly pronounced with the samples heated at 130 and 150 C up to the fourth hour of heating; further heating gave a gradual decrease in those two fatty acids. In the case of refined oil a slight temporary increase in linoleic acid was observed in the samples heated at 110 C, while in those heated at higher temperatures (130 and 150 C) the amounts of linoleic and linolenic acids showed a steady decreasing tendency. Similar quantitative changes in linoleic and linolenic acids were observed in the samples of hydrogenated oil.

The above results were confirmed by NMR analysis, which made it possible to establish quantitative changes in methine and methylene protons in α position to double bond. As established by GC analysis in the samples of refined oil heated at 110 C a temporary increase in unsaturation was observed (Tables 1–3, Fig. 2–3).

The increase in unsaturation was followed by a temporary decrease in *trans*-isomers (Table 4). The fact that

*To whom correspondence should be addressed at Academy of Economics in Poznań, Institute of Commodity Sciences, Ul. Marchlewskiego 146 150, 60-967 Poznań, Poland.

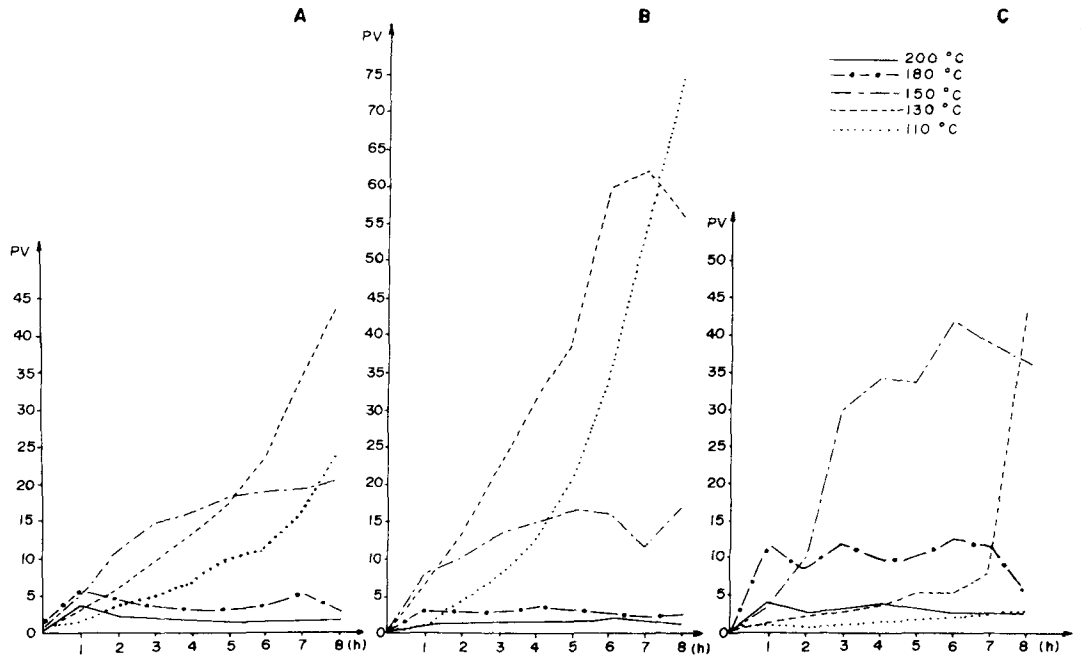

FIG. 1. Changes in peroxide value (PV) of (A), heated raw; (B), refined, and (C), hydrogenated rapeseed oils.

TABLE 1

Changes in Number of Methine and Methylene Protons of Heated Raw Oil

Heating time (hr)	Protons									
	110 C		130 C		150 C		180 C		200 C	
	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C
0	8.7	8.3	8.8	8.9	8.5	6.8	8.2	6.8	8.3	7.5
1	8.7	8.5	9.1	8.7	8.8	7.7	8.1	7.8	7.9	7.6
2	8.9	9.2	9.5	9.0	8.9	7.7	8.0	7.6	7.8	7.8
3	9.2	9.5	9.6	10.0	9.0	7.8	7.9	7.8	7.5	7.5
4	9.3	9.5	9.1	8.7	8.2	8.5	7.7	8.0	7.2	6.5
5	9.1	9.3	8.9	8.7	8.0	7.8	7.0	6.7	7.1	6.3
6	8.9	9.0	8.7	8.4	7.9	7.1	7.1	6.1	6.5	5.9
7	8.9	9.0	8.0	8.7	7.6	6.5	6.7	6.1	6.3	5.7
8	8.6	8.7	7.9	8.6	6.7	6.7	6.3	5.8	6.3	5.6

TABLE 2

Changes in Number of Methine and Methylene Protons of Heated Refined Oil

Heating time (hr)	Protons									
	110 C		130 C		150 C		180 C		200 C	
	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C
0	9.1	8.3	8.8	8.1	8.4	7.9	8.5	8.1	8.6	8.2
1	8.5	7.1	8.6	7.6	8.7	7.0	8.5	7.8	8.5	8.0
2	8.6	7.4	8.3	8.0	8.6	7.3	7.5	6.7	7.5	7.6
3	8.5	7.4	8.3	8.8	8.6	7.1	7.3	6.5	7.3	7.3
4	9.0	7.9	8.1	7.7	8.0	7.0	7.6	7.7	7.1	6.8
5	9.0	8.3	8.2	8.0	7.3	6.1	7.4	6.7	7.3	6.1
6	8.6	8.4	7.7	7.3	7.0	6.2	7.2	6.6	7.2	5.8
7	—	8.0	7.6	7.3	7.0	6.3	7.0	6.5	6.1	4.7
8	8.5	7.7	7.0	7.8	6.5	6.1	6.7	5.9	5.7	4.6

TABLE 3

Changes in Number of Methine and Methylene Protons of Heated Hydrogenated Oil

Heating time (hr)	Protons									
	110 C		130 C		150 C		180 C		200 C	
	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C	CH=CH	CH_2-C
0	6.8	7.8	6.1	7.4	6.3	6.3	6.1	7.6	6.0	8.6
1	7.0	8.1	6.4	7.8	6.3	7.0	5.9	7.0	5.5	6.5
2	7.2	8.2	6.5	8.5	6.4	7.4	5.8	6.4	5.4	6.9
3	6.8	8.7	6.1	7.6	6.2	7.0	5.8	5.8	5.4	7.1
4	6.7	8.0	5.9	7.6	6.0	7.0	5.6	5.6	5.3	7.6
5	6.7	8.7	5.2	7.2	6.0	6.5	5.2	5.2	5.0	7.7
6	6.7	8.0	5.6	7.0	5.3	7.6	5.0	4.9	5.0	6.3
7	6.7	8.1	6.0	7.5	5.1	6.3	4.6	4.5	5.0	6.0
8	6.6	7.9	6.4	8.2	4.9	5.9	4.5	4.3	4.9	4.4

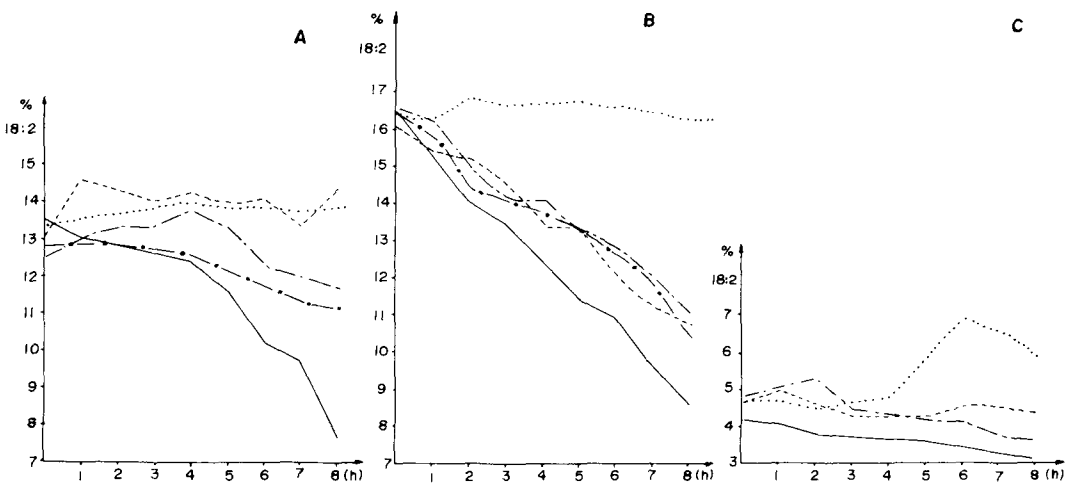

FIG. 2. Changes in the contents of linoleic acid (%) in (A), heated raw, (B), refined, and (C) hydrogenated rapeseed oils.

TABLE 4

Quantitative Changes in *Trans*-isomers of Fatty Acids During Heat Treatment[a]

Heating time (hr)	Temperature (°C)														
	Raw oil					Refined oil					Hydrogenated oil				
	110	130	150	180	200	110	130	150	180	200	110	130	150	180	200
0	2.2	2.5	2.1	2.6	2.5	12.4	12.2	12.6	12.9	12.7	40.4	41.0	41.5	40.5	40.2
1	2.5	2.0	1.3	1.2	4.2	12.2	11.7	8.9	13.5	12.5	37.0	40.5	43.0	42.0	38.2
2	2.5	1.6	2.2	1.8	8.6	11.8	11.5	10.2	16.1	13.2	33.2	46.0	40.2	40.4	37.0
3	2.8	2.2	3.5	2.0	8.3	12.1	11.6	12.0	17.5	13.9	45.3	40.8	40.3	37.4	35.5
4	2.3	2.3	4.3	4.3	9.0	12.2	13.1	14.3	18.3	15.6	40.0	41.0	41.0	36.0	32.0
5	1.3	2.0	4.8	5.1	10.3	12.7	13.7	14.8	18.9	20.5	40.2	40.1	40.0	34.2	37.0
6	2.0	2.6	5.6	7.2	11.8	13.2	16.2	16.3	21.1	22.6	40.6	40.3	33.2	35.0	38.0
7	2.9	3.0	7.2	7.2	14.2	14.1	21.0	16.9	21.5	23.2	41.3	38.0	30.8	34.8	38.6
8	3.5	3.7	9.5	9.3	15.3	14.8	21.9	20.7	22.0	23.4	40.1	36.2	28.3	35.6	38.2

[a]Percent of total fatty acids.

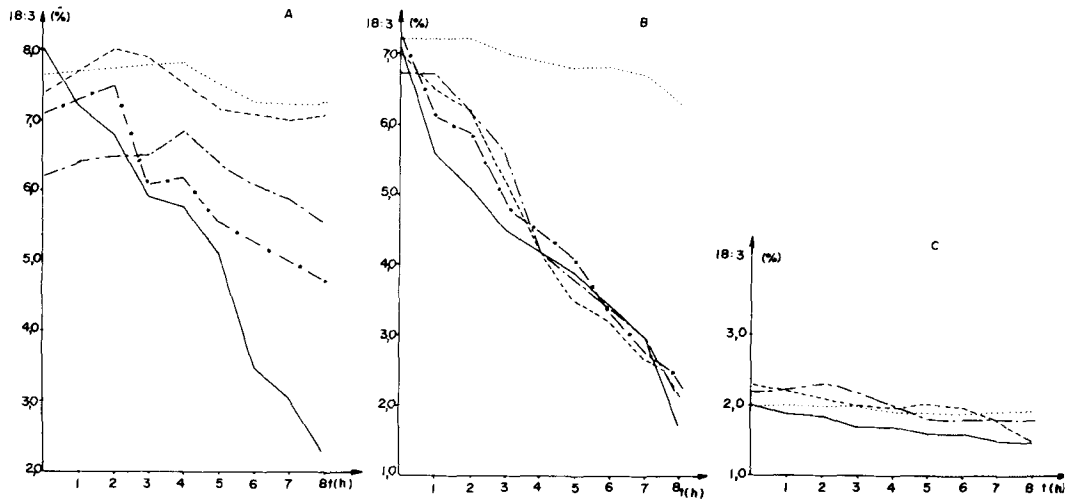

FIG. 3. Changes in the contents of linolenic acid (%) in (A), heated raw; (B), refined, and (C), hydrogenated rapeseed oils.

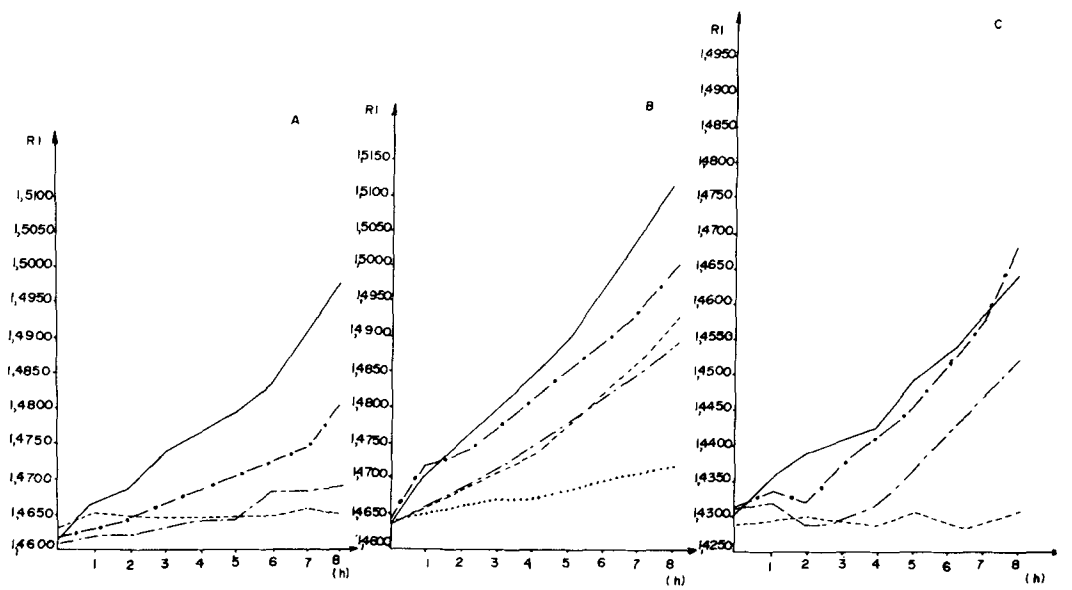

FIG. 4. Changes in refractive index (n_D^{40}) of (A), heated raw; (B), refined, and (C), hydrogenated rapeseed oils.

both changes were simultaneous and no polymerization occurred suggested an interrelationship between the concentrations of *trans* and *cis* isomers.

According to the results obtained, heating within the temperature range 110–150 C caused no substantial changes in the fatty acids of the oils, those that occurred seemed not to affect their nutritive value.

The changes in the samples heated above 150 C differed much from those described above. At 180 C and 200 C a drop in peroxides and polymerization were observed. Under these conditions the concentration of peroxides was inversely proportional to the rise in temperature. As the values of TBA test behaved similarly, the drop in peroxides resulted from the decrease in the rate of oxidation and not from decomposition.

In the samples heated at 150–200 C the dominating process was polymerization (Figs. 3–6). The character and extent of polymerization were found to depend considerably on the kind of oil. The samples of raw oil showed an increase in η and MMW > 3000, which suggested the formation of intramolecular polymers. The degree of polymerization in raw oil was lower than that in the two remaining oils. The samples of refined oil were found to accumulate high amounts of polymers (a considerable increase of η), their MMW values being lower than those for raw oil, however. As to hydrogenated oil, a relatively low increase in MMW was observed, this being accompanied by a more pronounced increase in viscosity, which might be due to the formation of intramolecular polymers. This supposition was supported by a decrease in

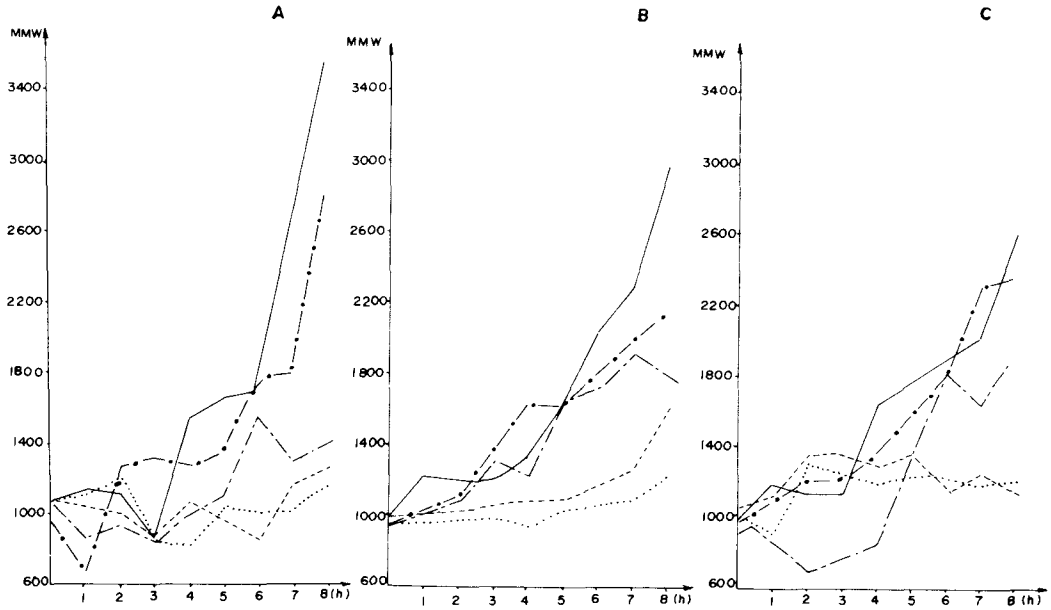

FIG. 5. Changes in mean molecular weight (MMW) of (A), heated raw; (B), refined, and (C), hydrogenated rapeseed oils.

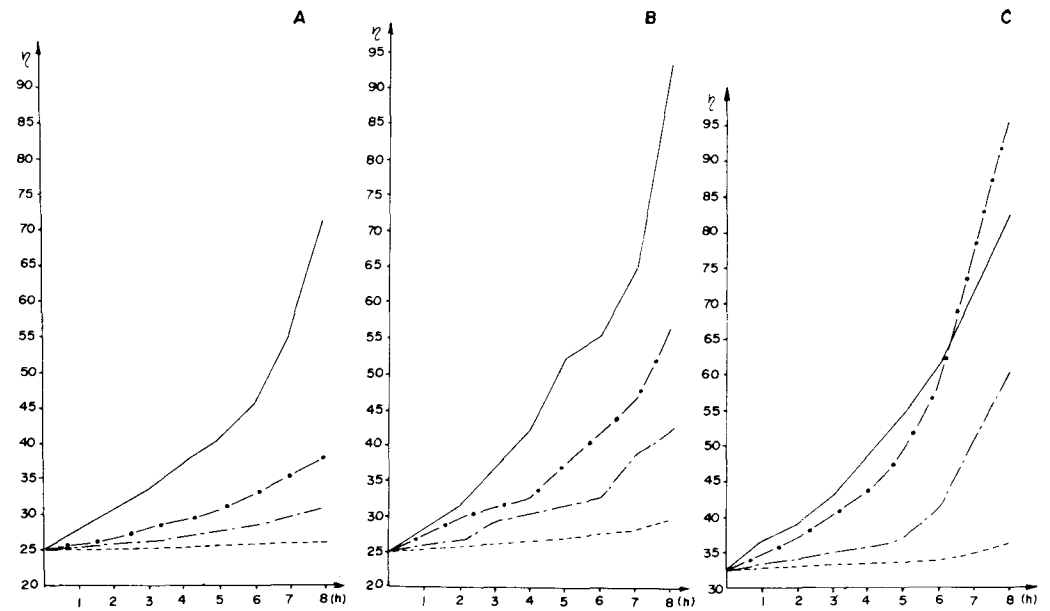

FIG. 6. Changes in viscosity (η) (cP) of (A), heated raw; (B), refined, and (C), hydrogenated rapeseed oils.

methylene protons at the carbons α to the double bons (δ 1.97 ppm) and methin protons (δ 5.27 ppm), where cross linkages might be formed. Independently of the kind of oil, some amounts of branched polymers might be formed; this was suggested by an increase in the number of CH_3 groups.

The *cis-trans* isomerization changes were highly differentiated (Table 2). On an eight-hr heating some increase in *trans*-isomers was evidenced in the samples of raw and refined oils. The samples of hydrogenated oil heated at 150, 180 and 200 C showed a marked decrease in *trans* fatty acids; at 150 C this decrease amounted to about 30%.

According to the authors' other data the temperature 150 C is optimal for decreasing *trans*-isomers in hydrogenated oils subjected to thermal treatment (8).

REFERENCES

1. Zalewski, S., and E. Brzozowska, *Roczniki Techn. i Chem. Zywn. 2*:225 (1972).
2. Kaunitz, H., R.F. Johnson and L. Pegus, *J. Am. Oil Chem. Soc. 42*:770 (1965).
3. Lang, K., *Fette, Seifen, Anstrichm. 76*:145 (1974).
4. Matsuo, N., *Symposium on Foods: Lipids and their Oxidation*, The Avi Publishing Co., Westport, CT, 1962, p. 360.
5. Perkins, E.G., *Food Techn. 14*:508 (1960).
6. Potteau, B., E. Biette and M. Lhuisier, *Ann. Biol. Au-im. Bioch. Biophys. 7*:59 (1967).
7. *Official Methods of Analysis*, Association of Official Analytical Chemists, edited by William Horwitz, Washington, D.C., 1975, Methods 28.022 and 28.052.
8. Leszkiewicz, B., and M. Kasperek, *Zeszyty Naukowe Akademii Ekonomicznej 134*:22 (1975).

[Received June 30, 1986; accepted March 30, 1988]