USE OF BROAD-LINE NMR TO DETERMINE THE AMOUNT OF SOLID PHASE IN COTTONSEED OIL HYDROGENATES

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The amount of solid phase in fats is generally determined by the dilatometric method [1]. However, this is inaccurate and has a number of defects [2, 3]. The use of broad-line NMR provides a faster and more accurate method for determining the amount of solid phase in a fat [4]. By means of NMR we have determined the amount of solid phase in cottonseed oil and hydrogenated samples 1 (on a Pd catalyst) and 2 (on Al–Ni–Cu). The iodine Nos. of samples 1 and 2 were 60.6% and 59.5% of I_2, respectively. The amounts of trans-acids in samples 1 and 2 were 29.5% and 21.6%.

The spectra were taken on a RYa-2301 instrument at a frequency of 40 MHz. The NMR signals were measured at temperatures beginning from 60°C, when the samples were completely molten, and every 10°C. The NMR signal consists of two lines. The narrow line corresponds to the liquid form of the molecules and the broad line is due to the presence of molecules in the solid state. The experimental values of the NMR signals were measured from the intensity of the peak, which was proportional to the amount of liquid phase [5].

The amount of solid phase was determined by comparing the signal of the sample at a temperature at which it was completely fused (60°C) with the signal of the sample at the given temperature [5]. In addition, we used another method of calculation which, from the NMR spectra taken at several temperatures, enabled us to determine the amount of solid phase in the sample at any given temperature [6]. As a standard we took the signal at 60°C. To find the liquid signal at another temperature the magnitude of the signal at 60°C was multiplied by a factor C_t calculated from the formula $C_t = 1 + (60 - t)(0.0308 - 0.00214\% \text{ H})$.

TABLE 1

T, °C	Amount of solid phase, %					
	cottonseed oil		sample 1		sample 2	
	comparison method	graphical method	comparison method	graphical method	comparison method	graphical method
30	None	None	—	6,5	—	4,6
25			5,8	9,6	3,3	6,9
20			—	14,8	—	10,9
15		3,2	—	19,9	—	14,9
10		4,2	20,7	29,6	19,1	22,6
5	—	14	—	36,8	—	32,7
0	12,2	21,5	48,4	52,2	38,9	41,5
−5	—	27.9	—	57,5	—	47,1
−10	29,8	35,3	67,4	68,8	52,5	54,5
−15	—	42.6	—	75.4	—	58,9
−20	45,2	51,4	78,3	79,1	61,4	62,8
−40	72	75,1	100	100	100	10,0

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By plotting a graph of the dependence of the measured and calculated peak intensities of the signals on the temperature the amount of solid phase was calculated:

$$\% \text{ of solids} = 100 - \frac{\text{sample signal at } t^\circ}{\text{calc. signal at } t^\circ} \cdot 100.$$

The results of the determination of the amount of solid phase by the two NMR methods are given in Table 1. It can be seen from the Table that the use of the comparison method gave somewhat lower figures for the solid phase content than the graphical method but with a decrease in the temperature this difference became smaller. In the range of temperatures from −10 to −40°C the two methods agree well. The divergence of the values in the regions of higher temperatures are due to exchange and dipole−dipole interactions of the resonating protons belonging to the liquid and solid phase. Under these conditions the contribution of the protons of the solid phase to the narrow signal in the liquid phase increases, which leads to exaggerated results. In the graphical method, however, the coefficient C_t automatically eliminates this error.

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